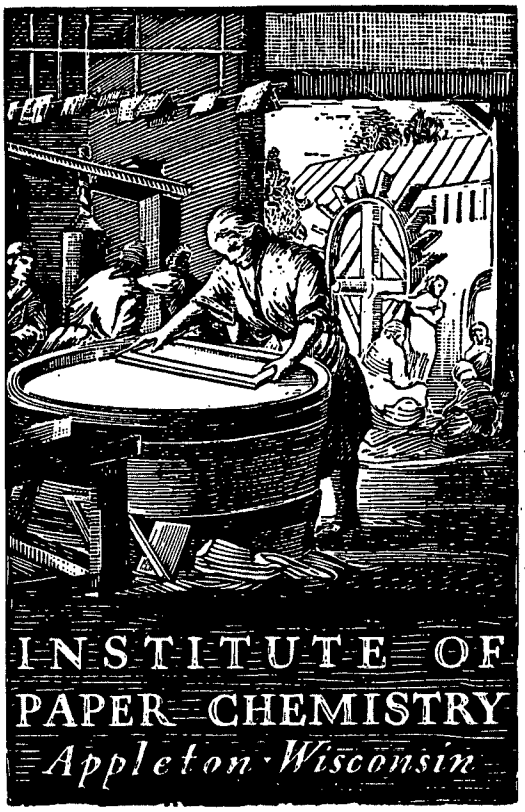

IMPROVING RETENTION OF PARTICULATE MATTER WHEN EMPLOYING RECYCLED WHITE WATER

Project 3245

Report One

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

August 25, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

Optimum retention of pulp fines, clay, titanium dioxide, etc., in recycled water is economically important to paper manufacturing for the recovery of material costs and water reuse, and yet the physical and optical properties of the paper must be optimized. Recycling may have adverse effects on these properties because of the buildup of the suspended and dissolved solids, and the temperature of the recycled white water. This project was created to investigate the effects of system closure on the complex interactions which occur between fibers, fines, filler particles, and other wet end additives.

This first progress report presents the findings on the role of pulp fines on the retention and optical properties of TiO_2 and filler clay with a bleached kraft northern softwood. Comparisons were made of results from handsheets made from a beaten pulp and a classified pulp, at consistencies approaching that in headboxes under controlled agitation. The white water from the first handsheet set was recycled to make a second handsheet set.

In the case of TiO_2, the presence of pulp fines is not a requirement for achieving good retention. The TiO_2 particles are attached to the fines, when present, and to the fiber walls in both pulps. The wall attachment, however, occurs on protruding fibrils which are essentially fines still bound to the fiber. The TiO_2 in the white water is attached to the fines. However, when the recycled pigment is retained in the subsequent handsheets, it appears well distributed over the fibers and fines, and it has excellent light scattering coefficients indicative of a small average particle size. This implies that the attachment forces between

the pigment and fines in the white water must be weak compared to the hydrodynamic shear forces of mixing and drainage. The retention of the white water recycled pigment is considerably lower than the initial retention, possibly for reasons of like surface charge on some fibrils and pigment.

In contrast to titanium dioxide, clay retention is very sensitive to the presence of pulp fines. The clay in the paper is nearly always associated with the fines, with very little bound on the fiber surface. The little clay retained with the classified pulp is on residual fines. The retention of clay with either pulp is reduced significantly by increasing the agitation. This indicates that the loss mechanism is primarily a direct response by the clay to the hydrodynamic shear forces rather than by loss on displaced fines. The clay in the white water is coagulated onto fines and with itself. Again, these coagulation forces must be weak compared to the hydrodynamic shear forces since the white water recycled clay retained in the subsequent handsheets has excellent light scattering coefficients indicative of a small average particle size.

In essence, both titanium dioxide and clay particles are retained through interaction with pulp fines. However, the platelike clay particles do not remain on the fibrils attached to the fiber surface presumably because they experience greater shear forces from mixing and probably weaker surface chemical forces than the smaller spherelike TiO_2 particles. Optimizing pulp fines retention is, therefore, an essential element in all papermaking systems.

The next phase of this work will examine the causes of retention loss in systems with hard water recycled many times. In addition, the understanding of the role of pulp fines will be broadened by selected studies using a bleached kraft northern hardwood pulp and a stone groundwood pulp of northern softwood.

INTRODUCTION

The paper industry has for many years made efforts to reduce freshwater requirements. A symposium on closing white water systems was held in 1953 (1). The Haynes report (2) of 1966 on 244 mills of all types indicates a range of water reuse depending on the type of mill from 13% to as high as 98% for a few non-integrated mills, with the average being 42%. A number of reports have considered methods of water reuse on paper machines (3-9). In general, the methods employed to effect reductions in freshwater intake involve good housekeeping, installation of equipment economical in using water, and use of savealls to recover solids and water for reuse (6). The economic benefits of white water reuse are discussed in these reports and summarized by Shema (10) as (1) conservation of freshwater, reducing treatment and capital investment costs; (2) conservation of raw materials and chemicals; (3) conservation of heat, reducing fuel costs in addition to providing more uniform operating temperature and faster drainage; and (4) reduced plant effluent, reducing the size of the treatment plant and thus the operating cost. In the future, stricter discharge water quality standards will encourage more and more mills to close their white water systems as completely as possible.

However, greater water reuse increases the dissolved and suspended solids, as well as the temperature in the machine system. These factors can present problems in operation, corrosion and erosion, scale formation, deposits, and biological problems (10). Clouse (4) lists problems normally encountered in water reuse as:

(1) Slime build up: clogs equipment, slows drainage, discolors sheet, produces odor and taste,

(2) Acid and salt increase: produces corrosion, affects sizing, wet strength, and color, affects paper strength and aging characteristics,

(3) Foam build up: slows drainage, contributes to slime, hurts formation,

(4) Pitch and/or beater size build up: deposits in the machine system and on the wires and felts,

(5) Starch and polymer build up: interfere with wire retention, upset saveall operation, contributes to slime and foam problems,

(6) Color change complications,

(7) Paper fines and colloidal particles build up: changing effect of hydration, drainage and sheet characteristics,

(8) Order changes: residual of white water to handle,

(9) Temperature increase: sizing decreases, slime inhibited or stimulated depending on the system, and

(10) Cost of reclamation.

There are a number of reports (11-16) of water closure in mills producing products with relatively few grades and few quality specifications. Two NSSC mills producing corrugating medium are described. Lowe (11) reports that, when the white water effluent flows dropped below 1,500 gal/ton and when dissolved solids in the white water were above 1.5%, problems became acute with respect to machine operation and maintenance, felt life, scaling and deposits, paper quality variability, chemical demand for sized and wet strength grades, and contaminants from waste paper. On the other hand Nelson et al. (14) report that the elimination of white water effluent brought operational and maintenance problems but these were solvable. They report that white water solubles increased from 0.9 to 3.7% and the increase permitted the reduction of fiber content for the same basis weight with no reduction in product

performance. The solubles, thus, do not build up to an unlimited extent, but are carried out with the product. Two waste paper mills producing corrugating medium and low grade papers are reported upon by Brecht et al. (12,13). In the first mill they report that the pH remained constant and the salt content became constant (10 times the original concentration) by virtue of carry out with the paper. No salting out of $CaSO_4$ took place. The machines ran faster because of higher temperature and the use of retention aids. The other operational problems were solved except for the slime which was controlled by thorough cleaning of dead spaces during weekly cleanup. In the second mill they reported similar results but did not need wire and felt cleaning aids, slime control agents or disinfectants because dead spaces had been eliminated. A retention aid was required. In both mills the corrosion problem was handled by use of stainless steel or PVC plastic as needed. Martin-Lof et al. (15) reported upon the water closure of a newsprint mill. They indicate that at least part of the normally discharged fiber fragments, fillers, and dissolved wood components can be recycled and included in the paper without detriment — optical and mechanical properties actually improved. They reported that the increased operating temperature reduced the slime. LeCompte (16) reported upon a tissue mill with 87% water recycle. The increase in soluble organics was not significant but the increase in soluble inorganics had to be controlled by bleed from the system.

An important step in these closures was to achieve increased retention of the suspended solids on the wire. This increases drainage by increasing the freeness in the headbox and it increases the saveall efficiency by lowering the suspended solids in the white water (17). Martin-Lof (15) stated that anything with retention over 50% will not build up in the white water.

In the case of white papers, Aldrich (18) presented the results of a 1971 survey by Western Michigan University of 85 fine paper mills with 185 machines. On 44% of the machines surveyed efforts were made to close the system so that water use was less than 5000 gallons/ton, and an additional 34% were using less than 10,000 gallons/ton. A majority reported no problems due to circuit closure, but the following few problems were encountered (percentage based on the total number of machines): slime increase (17%), poorer paper quality, particularly dirt (12%), increased felt filling (9%), increased corrosion (4%), and reduced sizing (5%). It was noted that many contradictions appeared. The average one pass retention of suspended solids was estimated to be about 70% and to change only about 2% with high closure. However, the spread of values was from 30 to 90%. It was noted also that the retention was a function of basis weight and machine speed. On the other hand, Lodzinski (19) has analyzed 67 mass balance data sets from 16 different machines in 7 different mills. The white water closure ranged from 83 to 100% with a typical value of 96%, and the one pass retention of ash ranged from 2 to 70% with a typical value of 23%. The one pass retention decreased exponentially with increasing headbox ash depending on the ratio of machine speed to basis weight and likewise exponentially with increasing sheet ash. Thus, high ash concentration contributes to poor retention directly. It is evident that many machines do have a single pass filler retention problem and complications occur with recycling.

Two experimental machine trials of a closed system on fine paper have been reported (20,21). Lewis and Bowman (20) evaluated a special $CaSO_4 \cdot SiO_2$ pigment filler in a 5-day closed system run on the University of Maine fourdrinier (12 inch trim, 50 ft/min). The mass balance retention value of the added filler remained constant at 90% indicating that the water closure was effective only to

that extent. The degree of sizing and bursting strength decreased steadily as the free acid and sulfate increased in the white water in the first 2 days while other sheet properties remained steady. The special pigment was then added to replace some of the TiO_2 and the burst and sizing improved. They concluded that the acid was the cause of the problems. They observed no slime problem, perhaps due to the high temperature (80°C). Aldrich and Janes (21) studied the effect of water closure on fine paper by employing three continuous 3 to 5 day runs on the Western Michigan University fourdrinier (20 inch trim, 60 ft/min). The closure went from 72 to 97% (only the press water was discharged) and gave the following benefits: savings of 18% in fillers, 50% in alum, 20% in rosin, and 50% reduction in BOD_5 in effluent. They found no significant differences in paper strength, suspended solids, felt filling, dirt in paper, or printability. The paper was made effectively at 1,200 gal/ton. The dissolved solids rose from 0.06% and leveled off at 0.19% after 4 days. The sulfate content remained about constant in contrast to their earlier closed run and to mill experience normally reported. The growth of slime increased at 110°F but slime was almost eliminated at 125°F. The single pass retention (70%) decreased only 2% on closure and the average optical properties of the paper remained constant. Because of the relatively slow speed, it is difficult to compare these results with production fourdriniers.

In white papers high single pass retention of suspended solids is vital for efficient recovery of added pigment, for high freeness in the headbox, for efficient saveall operation and for high one pass retention. As white paper mills increase water reuse approaching complete closure the build up of materials in the white water, such as starches and sulfate, could lead to reduced filler retention, particularly on the fast, high production machines, in integrated mills. Maximum retention of colloidal material must be achieved with control of chemical build up.

This project was created to investigate the effects of system closure on the complex interactions which occur between fibers, fines, filler particles, and other wet end additives. The objectives are: (1) to establish the controlling phenomena affecting the retention of particulate matter, (2) to determine those major factors which cause variability in the retention, and (3) to establish methods of retention control and maximization.

The program has a total budget of $170,000 over a two-year period starting October 1, 1974.

There have been many single-pass retention studies of TiO_2 and fines such as Williams et al. (22-24) from which hypotheses on retention and optical behavior are evolving. These studies show that retention of particulate material by pulp in a papermaking furnish is achieved through creation of favorable flocculating conditions by reducing the stabilizing effect of the electric double layer of the surfaces or by producing polymer bridges between surfaces.

Since particulates not retained on the initial cycle may undergo additional flocculation to larger agglomerates, their retention and optical characteristics may change in subsequent cycles. Furthermore, it is possible that the agglomerates will be covered with pulp fines which will, in turn, control the surface properties. [Pulp fines are defined here as any organic component of the pulp in the aqueous dispersion which passes through a screen of selected mesh (e.g., 150 mesh). This includes settleable components, near soluble components, and colloidal solubles.] Subsequent retention of the agglomerates would thus be determined by conditions favorable to fines retention. This hypothesis is supported by the observation that pigment remaining in the white water always appears to be associated with extraneous material (25). Thus, the effect of pulp fines is an initial concern.

In brief, the program is being carried out in four phases:

I. The role of fines in the retention of recycled particulates,

II. The causes of retention loss,

III. Means of improving retention, and

IV. The factors causing variations in the optical properties, and methods of control.

The work of Phase I is presented in this first progress report. The effects of pulp fines on the retention and optical behavior of titanium dioxide and of filler clay, using recycled white water, have been evaluated by comparing results obtained using pulps with and without fines. Handsheets of bleached kraft northern softwood pulp with TiO_2 or filler clay were made at consistencies approaching those found in headboxes. Agitation was controlled and alum was used at pH 5 as the retention agent. The white water from the first handsheet set was collected and recycled to make a second set of handsheets. The filler retention, optical properties, filler location in the handsheet and white water, electrokinetic state of the particulates, fines loss, and alum distribution were then determined for both sets of handsheets.

RESULTS AND DISCUSSION

TITANIUM DIOXIDE

Titanium Dioxide Retention

The effect of alum concentration at pH 5.0 on the titanium dioxide retention is shown by the data presented in Fig. 1 for the two pulps. Both pulps show the same maximum at about 3×10^{-5} molar alum. The range of alum concentrations used in this TiO_2 study are in the vicinity of this maximum. Beyond the maximum the decrease in retention with increasing alum concentration has been observed before (25) and is probably due to the increasing positive charge of both pigment and pulp. The classified pulp has a much more pronounced decrease possibly from a greater positive charge effect.

The retention results for both pulps are presented in Table I for the variables of pigment loading (5 and 15% based on fiber), consistency (0.1 and 0.3%), agitation (70 and 140 oscillations expressed in units of cycles per minute, cpm), and handsheet cycle. The alum concentrations are expressed in terms of percentages based on dry fiber present since, as will be shown, most of the alum is adsorbed by the pulp at consistencies higher than 0.1%. The adsorbed alum causes the collapse of the electrical double layer thus the cationic concentrations are unimportant. The sensitive retention response of the classified pulp system noted in Fig. 1 and seen in the data in Table I at 0.1% consistency, and the zeta potential data, shown later, support this choice for expressing the alum concentration. [The 3×10^{-5} molar alum is equivalent to 0.6% alum for 0.3% consistency and 2.0% alum for 0.1% consistency, and 1×10^{-5} molar alum is equivalent to 0.6% alum for 0.1% consistency.]

TABLE I

THE RETENTION[a] OF TITANIUM DIOXIDE PIGMENT BY BLEACHED KRAFT NORTHERN SOFTWOOD

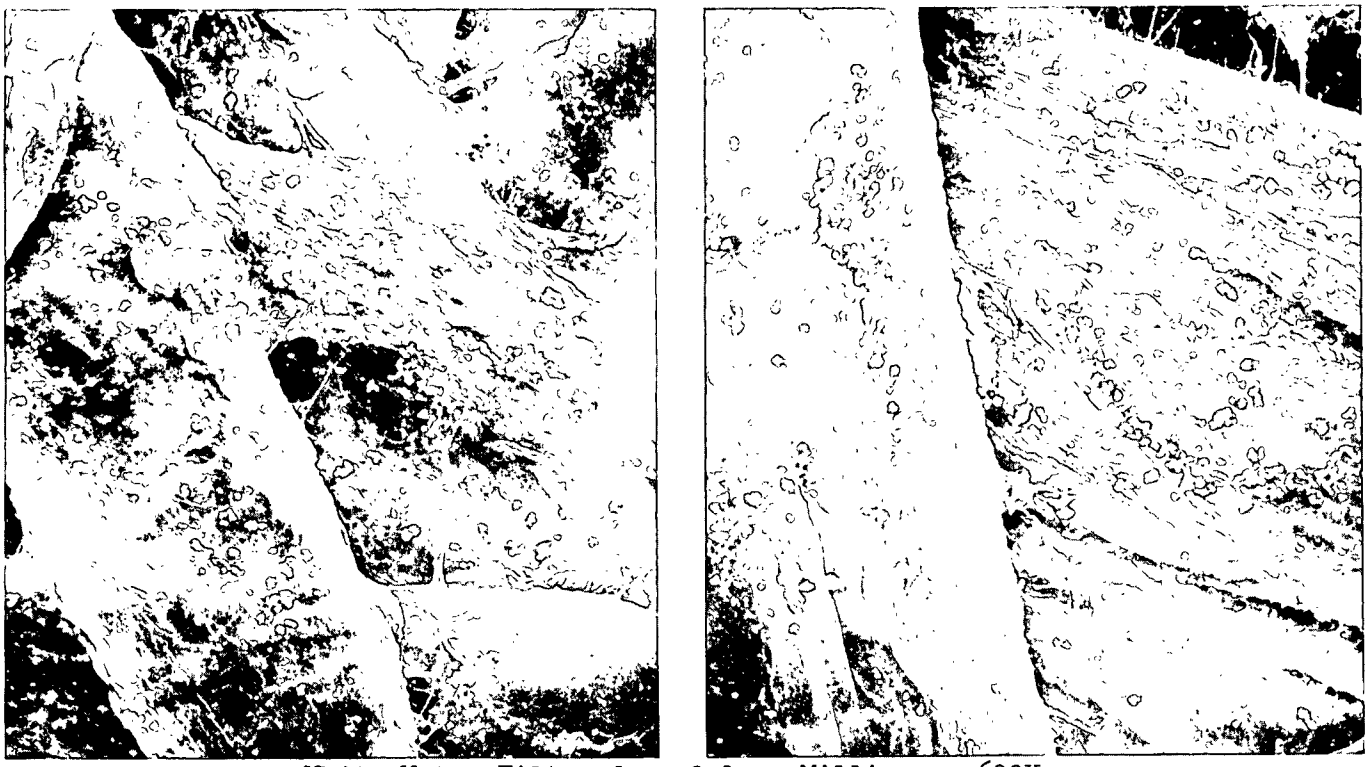
	445 CSF Pulp									Classified Pulp								
TiO_2[b], %:	0			5			15			0			5			15		
Alum[b], %:	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0
First Cycle Handsheets																		
Consistency, %							70 cpm[c]											
0.1					62	63		70	69					57	48		67	46
0.3				7	69±3			78±3					3	68±2			67±2	
							140 opm											
0.1					59	62		60	58					60	47		59	62
0.3					68±1			72						62			68	
Second Cycle Handsheets																		
							70 cpm											
0.1					38	50		53	53					34	34		37	29
0.3				5	37			55					8	45			37	
							140 cpm											
0.1					42	53		45	46					32	36		38	17
0.3					49			52						40			48	

[a] Defined as the percentage of the weight of TiO_2 in the furnish for that cycle. The level of replication is indicated where duplicate runs were made.
[b] Based on OD weight of pulp.
[c] The agitator oscillates at a rate given in cycles per minute.

445 CSF

Classified

Handsheet, 2500X



White Water Filtered on 0.1 μm Millipore, 600X

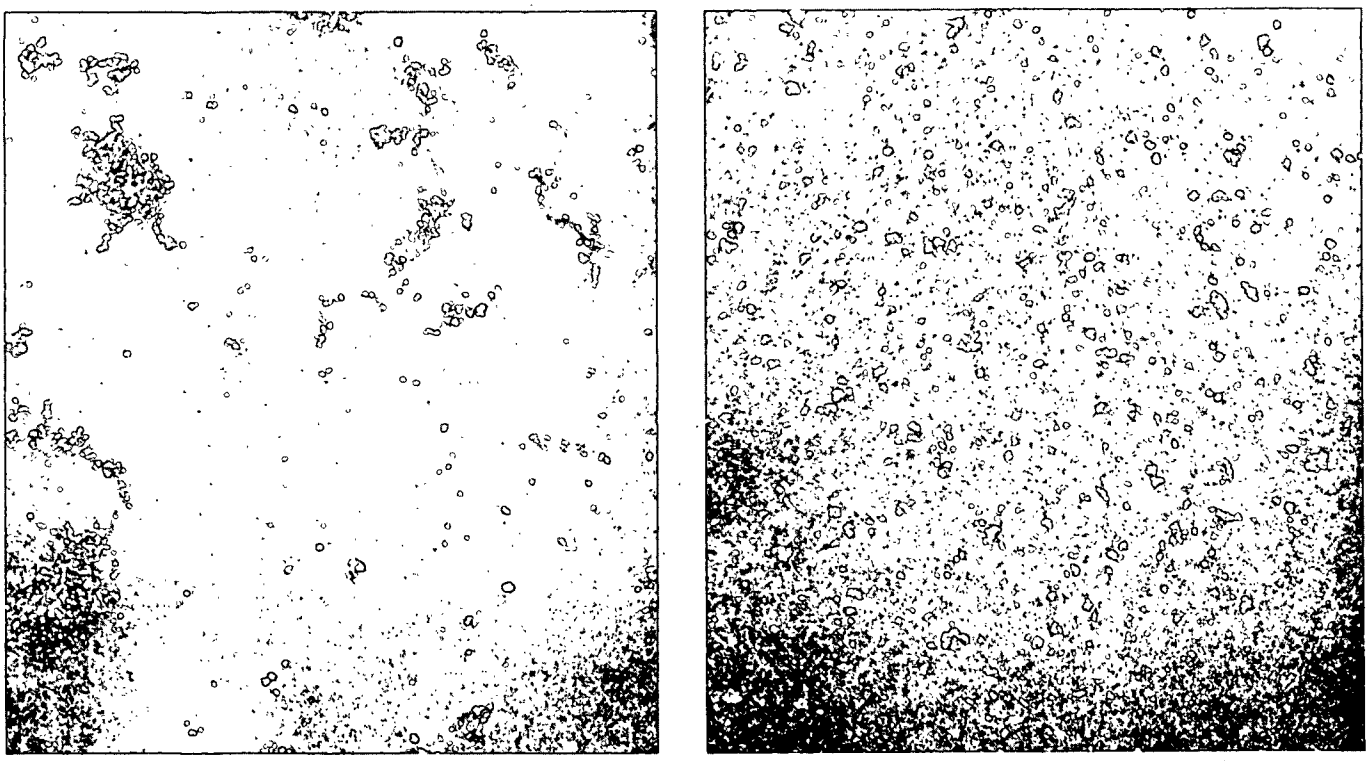


Figure 2. Scanning Electron Micrographs from the Systems with Titanium Dioxide. Furnish Conditions 0.3% Consistency, 0.6% Alum, pH 5, 5% TiO_2, and 70 cpm

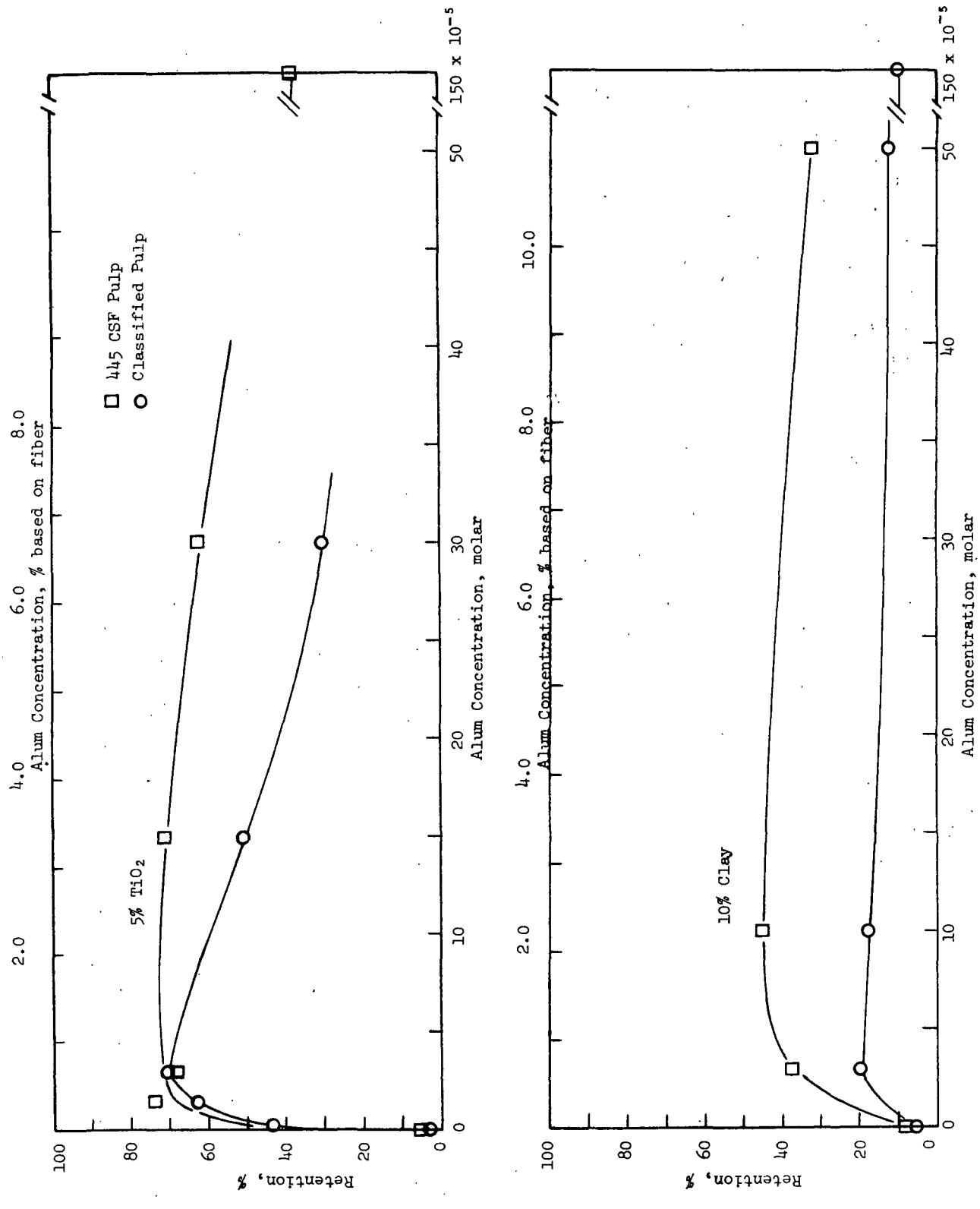


Figure 1. The Retention of Filler vs. Alum Concentration at pH 5, 0.3% Consistency, and 70 cpm

The first thing noted is that in the absence of fines only a small decrease in the retention occurs when comparing the same conditions of the two pulps in the first cycle. Scanning electron microscopic (SEM) examination of handsheets revealed that the pigment was retained on the fines, when present, and on the surface of the fibers of both pulps. Figure 2 shows representative micrographs. Previous work (22) has shown that in the wet state the TiO_2 retained on fibers is essentially all attached to protruding fibrils. Although not readily apparent in Fig. 2 because the fibrils have collapsed during drying, close examination reveals many pigment particles are attached to fibrils which extend from the fiber surface. If these fibrils can be thought of as "fines" still attached to the fiber, then the retention of pigment still takes place on these "fines," even though the usual fines may be essentially absent. Thus the loss of pigment through normal fines loss in the classified pulp system is important only to the extent of the distribution of pigment between fines and fibers. This is dependent on the hydrodynamic area per unit mass of pulp presented by each. In the classified pulp, containing very few fines, the pigment loss from fibers must be by hydrodynamic shear forces. In like manner these shear forces must also contribute to the slight pigment loss observed for some conditions in the 445 CSF pulp system.

In the first cycle the retention results show only slight, but generally consistent, increases with increasing consistency and decreasing agitation for given pulp and alum conditions. Both responses are commonly experienced and are due to the increasing pigment-fiber collision probability and to decreasing hydrodynamic shear, respectively (23). The retention increases slightly with increased pigment loading when comparing systems with the same pulp, consistency, alum concentration, and agitation. This nearly constant retention regardless of loading is consistent

with earlier findings (25) and suggests that the capacity for the fibers and fines to retain pigment has not yet been affected at even the highest loading.

Presented in Fig. 3 and 4 are the zeta potentials of the colloidal solids in the white water of the two pulps. (See Appendix, Tables XIII and XIV for data.) The zeta potentials are essentially independent of agitation and recycling. When the fines are present (445 CSF) the particles respond for the most part like pulp fines. This has previously been noted by McKenzie (26). Figure 2 also presents SEM micrographs of the suspended solids in the white water. The pigment particles are seen to be associated with the fines when the latter are present. When the fines are absent, the pigment particles in this alum-containing furnish are strongly positive and in a reasonably good state of dispersion. As the pigment content increases, the fines-pigment agglomerate produces a more positive zeta potential. This would be expected when the alum-produced cationic pigment and the anionic pulp fines are combined. For the 445 CSF pulp the fines are still negative at 2% alum concentration, so the cationic pigment is retained well at both 0.6 and 2% alum. For the classified pulp, the residual fines are negative at 0.6% alum but positive at 2% alum. Accordingly, the cationic pigment is retained well at 0.6% but significantly less at 2%. The sensitivity of retention to the colloidal conditions is again confirmed.

The retention in the second cycle was significantly less than in the first cycle for all data sets. SEM micrographs of the second cycle handsheets looked the same as those given in Fig. 2 for the two pulps. This means that in the case of the 445 CSF pulp the pigment must be only weakly attached to the fines in the white water, as the retained pigment in the second cycle handsheets is again distributed quite uniformly over the fiber surfaces. If the fines-pigment agglomerates in the white water remained intact during subsequent sheet formation, the

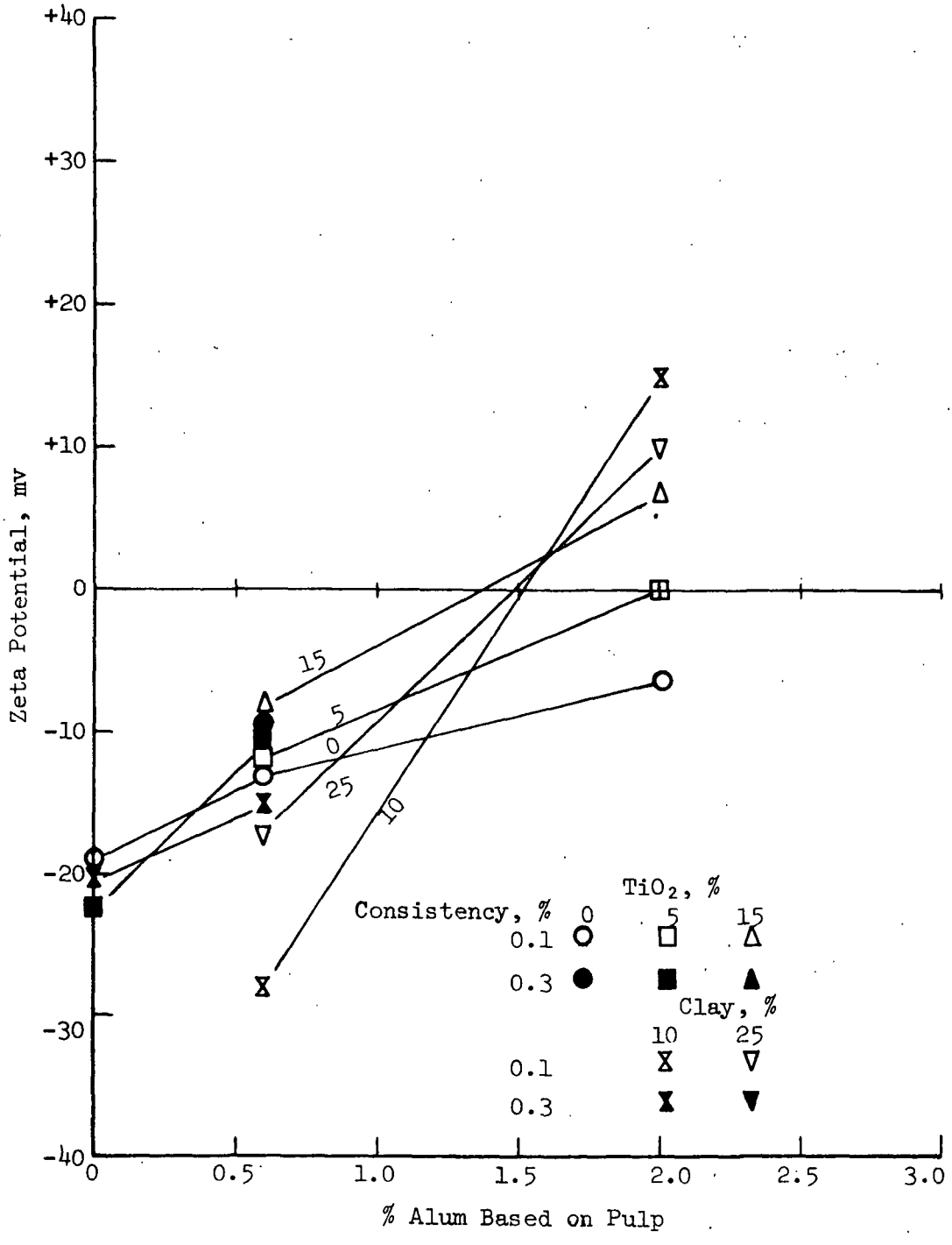


Figure 3. The Zeta Potential of the Suspended Solids in the 445 CSF Pulp White Waters

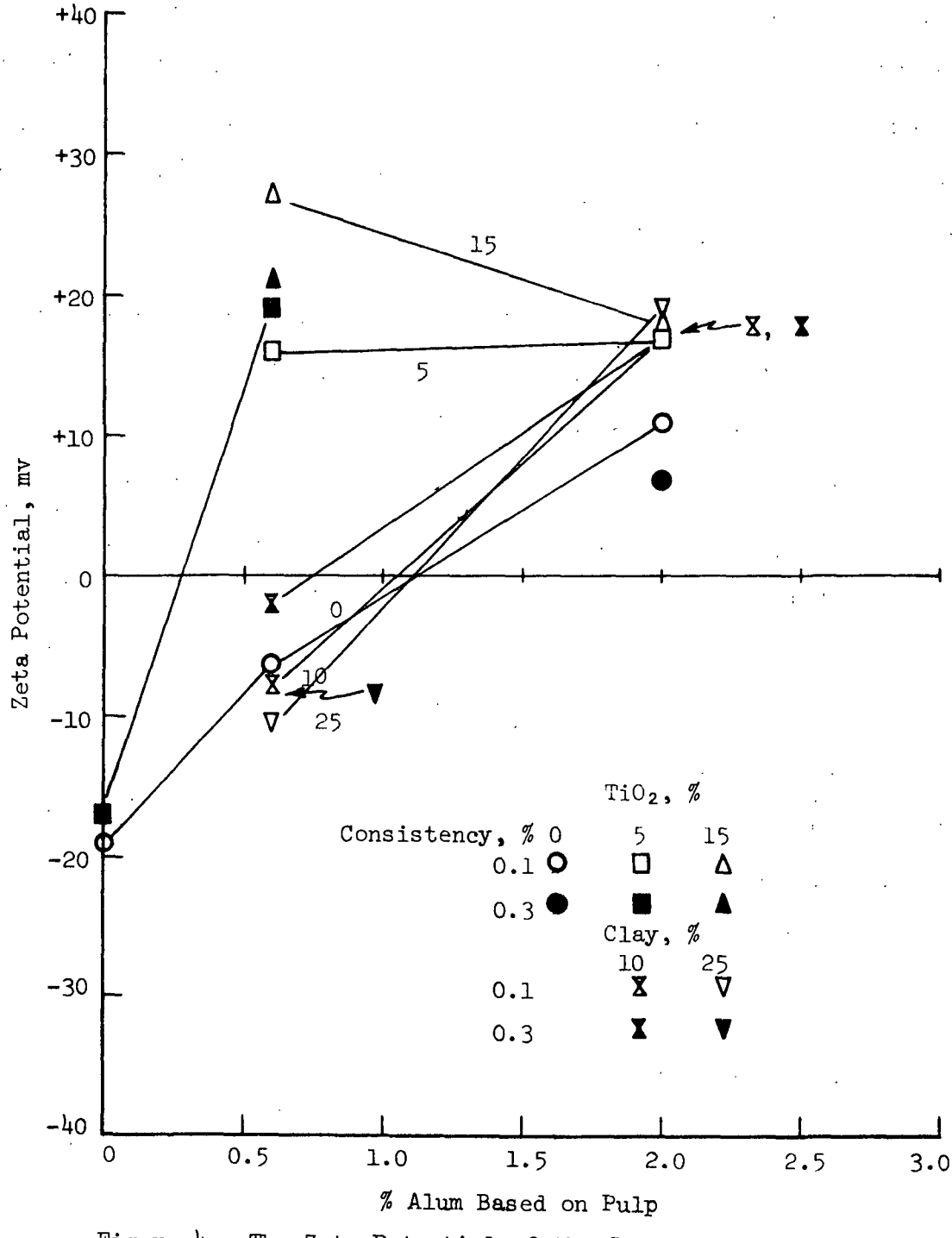


Figure 4. The Zeta Potential of the Suspended Solids in the Classified Pulp White Waters

separation distance between the pigment particles would be unchanged. The micrographs, however, indicate that the particles in the sheet are more widely separated than is observed in the white water. This redistribution which occurs during mixing must arise from either pigment redispersion or from pigment particle transfer during fiber-fines collisions.

The cause of the retention loss in the recycled system is not readily identified. The optical data presented later indicate that the average particle size of the retained recycled pigment is even smaller than the first cycle. Thus the reduction in retention does not appear to be due to an increase in the particle size. The zeta potentials of the colloidal material in the second cycle white water are similar to those of the first cycle. This suggests that the alum addition in the second cycle has not changed the surface charge of the recycled pigment, which is surprising. Possibly the retained pigment had a zeta potential different from that remaining in the white water. It may be that a portion of the pigment is incapable of being retained, regardless of the alum consistency and shear conditions. If so, it would be an increasing fraction of the pigment in each cycle and would cause the retention, based on the total pigment present, to decrease with each cycle.

In the second cycle retention data for the 445 CSF pulp, the influences of alum concentration, consistency, pigment loading, and agitation are about the same as observed for the first cycle data. However, for the classified pulp the inconsistent data are more numerous. Some of this inconsistency is believed to be due to the poorer sheet formation when using the classified pulp.

Pulp Fines Loss

The results concerning the pulp fines lost during handsheet formation are presented in Table II, for both pulps. The loss is expressed as a percentage by weight of the pulp present in the furnish which remains in the white water and can be filtered out of the white water onto a 0.1 μm millipore filter. The values of 2 to 3% for the 445 CSF pulp appear to be low; however, the use of the fine (100 mesh) wire for sheet formation has controlled the upper size limit of the fines. The classified pulp has just detectable losses of pulp as anticipated.

In looking at the 445 CSF pulp data, several things become evident. First, the alum concentration does not affect the pulp loss. Thus the electric double layer repulsions are not of consequence for pulp fines in these systems. This indicates that the hydrodynamic shearing forces on the fines are larger than the net attractive forces between pulp fines and fibers since surface charge effects have been found to affect fines retention (23). Next, as anticipated, increased agitation causes a small increase in fines loss and increased consistency causes a small decrease in fines loss. Also, the quantity of fines lost in the second cycle is less than twice that in the first cycle indicating that many of the recycled fines are retained in the subsequent cycle. Finally, the fines loss in the first cycle in general increases with pigment loading. This is also evident when viewing the classified pulp data at the lowest consistency (0.1%) where retention by the sieving mechanism is least possible. This loading effect might be due to the net electrokinetic property imposed on a pulp fine by the attached pigment.

Optical Properties

Presented in Fig. 5, 6, 7, and 8 are the light scattering coefficients of the handsheet sets presented in Table I vs. the sheet pigment content. These

TABLE II

PULP FINES LOST[a] IN TITANIUM DIOXIDE CONTAINING FURNISHES OF BLEACHED KRAFT NORTHERN SOFTWOOD

	445 CSF Pulp									Classified Pulp								
TiO_2[b], %:	0			5			15			0			5			15		
Alum[b], %:	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0
First Cycle Handsheets																		
Consistency, %	70 cpm[c]																	
0.1		1.4	1.6		2.1	2.1		2.5	2.4		0.3	0.1		0.3	0.6		1.2	1.1
0.3	1.8±0.3	1.9±0.2		1.9±0.0	1.6			1.6±0.1		0.2±0.0	0.4		0.3±0.1	0.3±0.0			0.2	
	140 cpm																	
0.1		2.2	2.1		2.3	2.4		2.6	2.5		0.2	0.2		0.7	0.5		1.2	1.5
0.3	1.9	1.7			1.9±0.1			2.2		0.1	0.2			0.4			0.4	
Second Cycle Handsheets																		
	70 cpm																	
0.1		2.6	2.8		4.2	2.6		2.8	2.9		0.2	0.1		0.5	0.6		0.8	1.1
0.3		2.0±0.1		2.7	1.8			1.9			0.3		0.1	0.3±0.1			0.3	
	140 cpm																	
0.1		2.7	2.9		2.9	2.9		4.4	3.4		0.2	0.1		0.7	0.6		0.6	0.6
0.3		2.2			2.2			2.4			0.2			0.3			0.2	

[a] Given as the percentage of the OD weight of the pulp in the furnish. The level of replication is indicated where duplicate runs were made.
[b] Based on OD weight of pulp.
[c] The agitator oscillates at a rate given in cycles per minute.

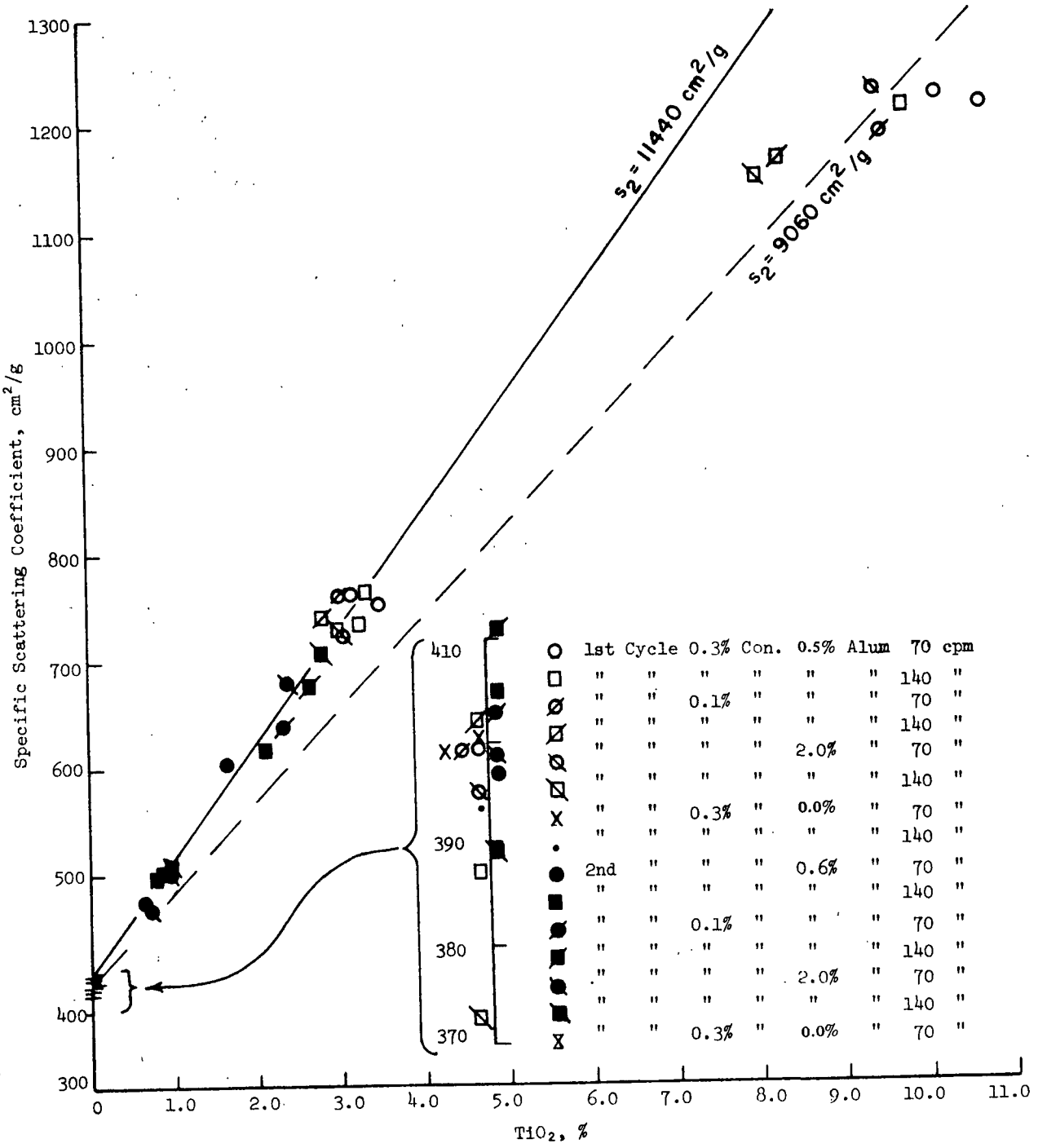


Figure 5. The Specific Scattering Coefficients vs. TiO_2 Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 457 μm

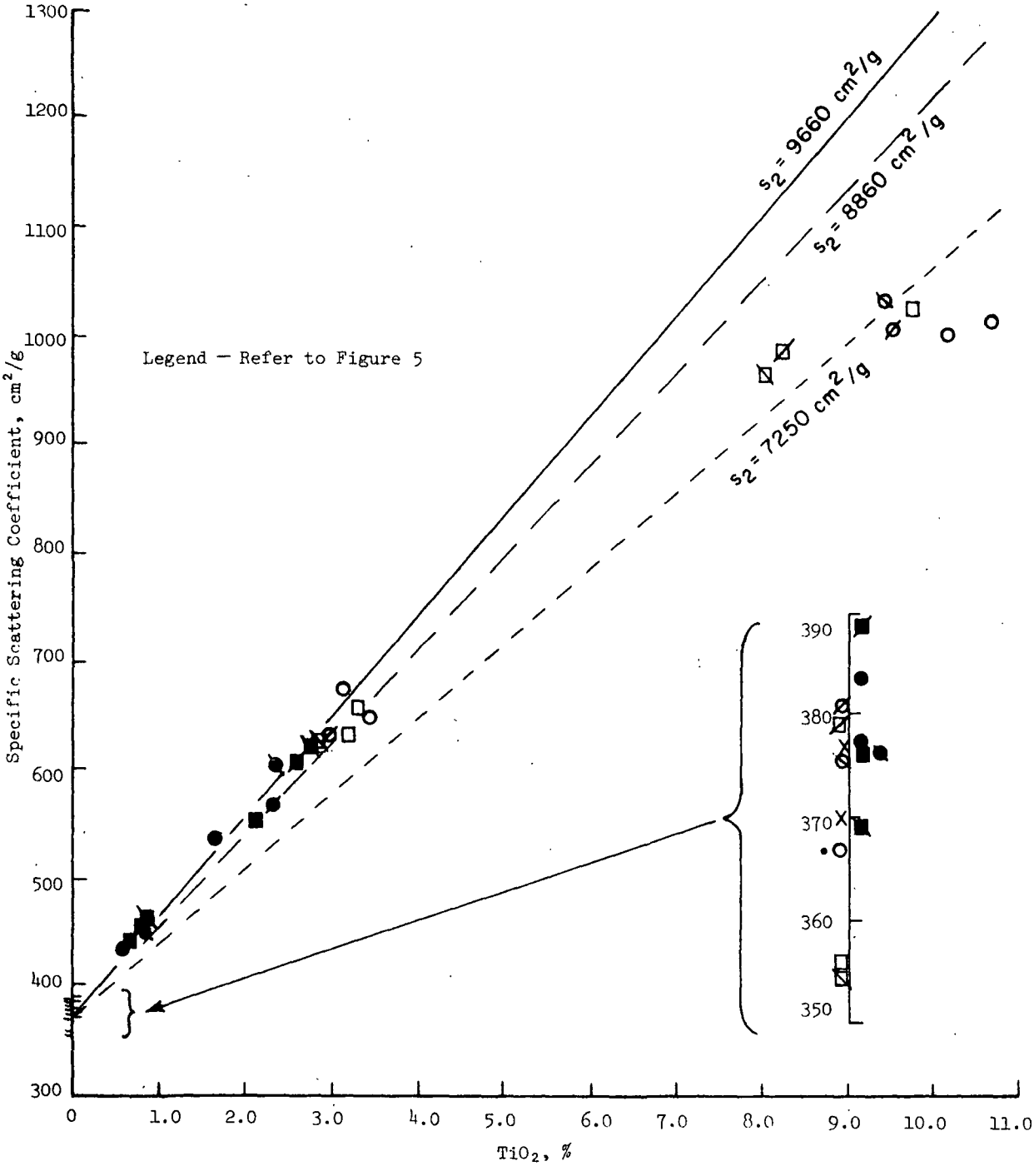


Figure 6. The Specific Scattering Coefficients vs. TiO_2 Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 572 μm

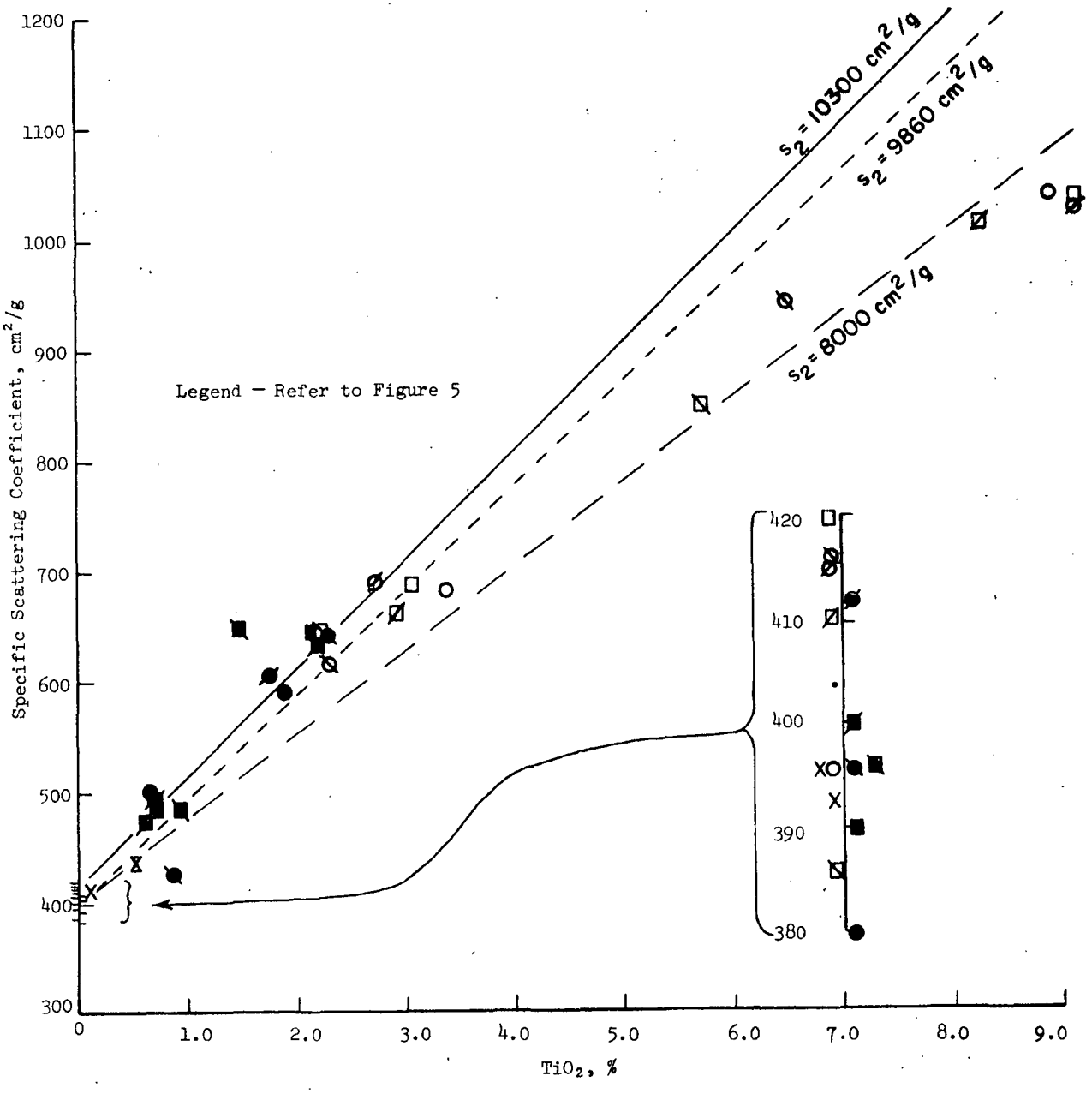


Figure 7. The Specific Scattering Coefficients vs. TiO_2 Content of the Paper for Classified Pulp Using Light of Wavelength, 457 μm

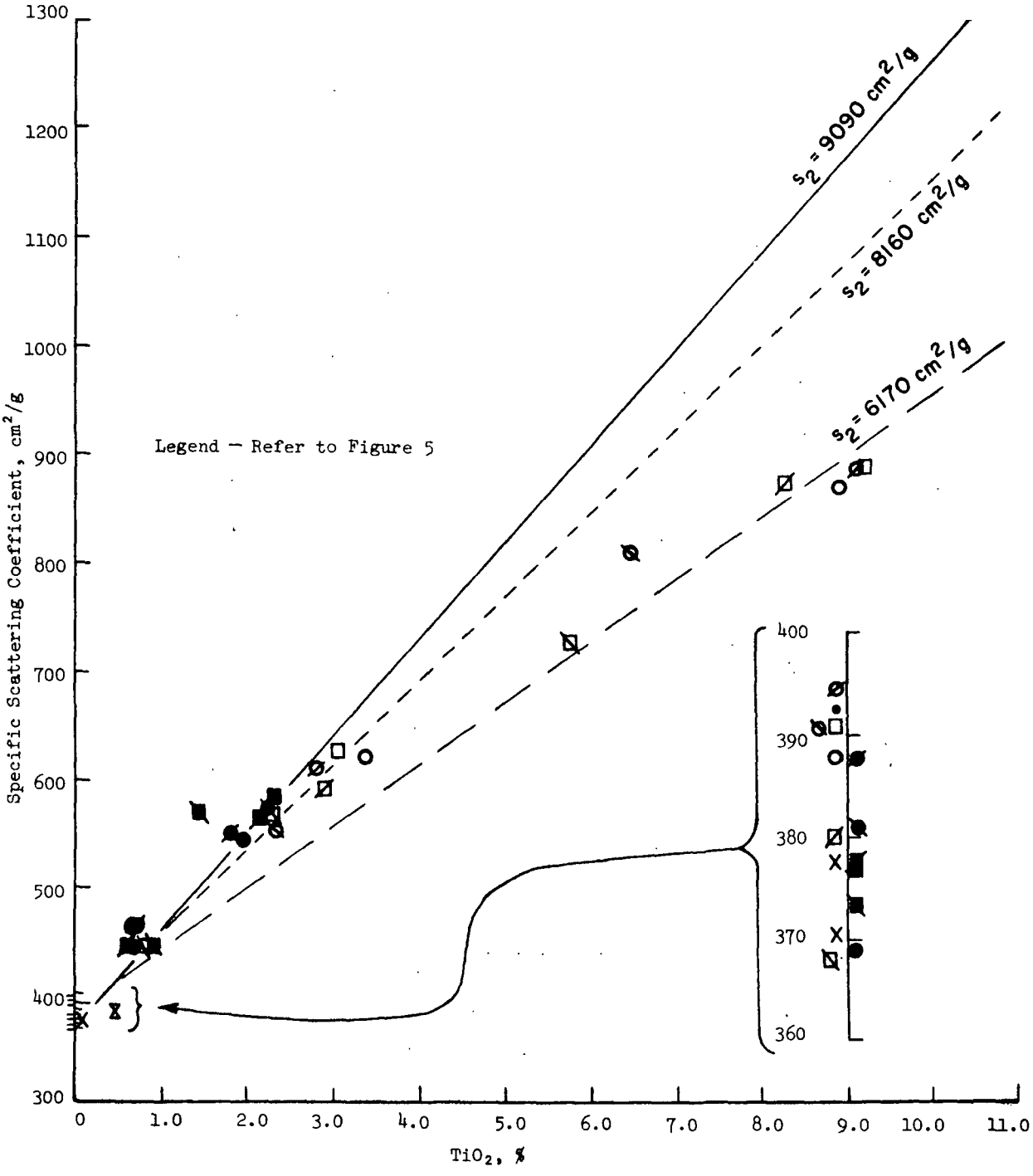


Figure 8. The Specific Scattering Coefficients vs. TiO_2 Content of the Paper for Classified Pulp Using Light of Wavelength, 572 μm

data are for the two pulps measured at two wavelengths, 457 and 572 μm, the spectral maxima for brightness and opacity measurements, respectively. If the scattering coefficients of the pigment and the pulp remain unchanged with increased pigment content, the function should be linear as expressed by the equation

$$s = s_1 + (s_2 - s_1)f_2, \qquad (1)$$

where s, s_1 and s_2 are the specific scattering coefficients of the paper, the pulp and the pigment, respectively, and f_2 is the weight fraction of pigment in the sheet (29). The specific scattering coefficient is a sensitive inverse function of the average size of the light scattering material.

The data for the first cycle are not linear but depend on the loading level of the pulp. The classified pulp is much more pronounced in this effect. This nonlinear behavior at high pigment loadings results from an increase in the average particle size as a result of self flocculation of the pigment. With no fines present, the self flocculation probability is increased. A straight line through each pigment loading data set was used to calculate a mean s_2 for that set of data.

The data for the second cycle from both loading level conditions form a straight line with a slope equal to or greater than those from the first cycle. [In all cases the actual quantity of pigment remaining in the white water from the first cycle which is thus available for retention in the second cycle is less than 5% based on added fiber, a value equal to or less than the lower initial loading level.] This indicates that the pigment retained from the recycled white water has an equal or smaller average size than that retained in the first cycle. The recycled flocculated pigment was redispersed in the subsequent furnish. This is a surprisingly favorable result. These pigment scattering coefficients are on the

high end of the values usually reported in the literature (27-30) indicating that the retained pigment is of small average size and evenly distributed.

Since the optical measurements usually are accurate to within a few percent, the small spread of the data must stem from factors affecting sheet structural differences caused by the changes in alum, consistency, and agitation. The greater spread in the classified pulp data is likely a result of the poorer formation of the handsheets from this pulp. It is of interest to note that the two pulps have about the same scattering coefficient, in spite of about a three fold difference in their hydrodynamic specific surface areas. Their internal fiber areas available to light scattering are similar when dried. This is typical of many coniferous chemical pulps due to fibrils collapsing onto the fiber during drying (31). The pulp fines added on recycling are of little consequence here.

In a similar manner, the light absorption coefficients of sheets should be a linear function of the pigment content as $\underline{k} = \underline{k}_1 + (\underline{k}_2 - \underline{k}_1)\underline{f}_2$ where $\underline{k}$, $\underline{k}_1$, and $\underline{k}_2$ are the specific absorption coefficients of the paper, the pulp, and the pigment, respectively. The absorption data are presented in Fig. 9 and 10. The slopes are almost zero, indicating that the pigment has an absorption coefficient about the same as the pulp. The values of the absorption coefficients are similar to those reported by Schwalbe (29). The absorption coefficient for the 445 CSF pulp increases significantly from the first cycle to the second cycle and yet the scattering coefficient was found to be unaffected on recycling. The classified pulp shows only a slight increase in the absorption coefficient. This indicates that the fines carried in the white water and retained in the subsequent cycle add color to the pulp. The source of this color is probably the lignin in the fines.

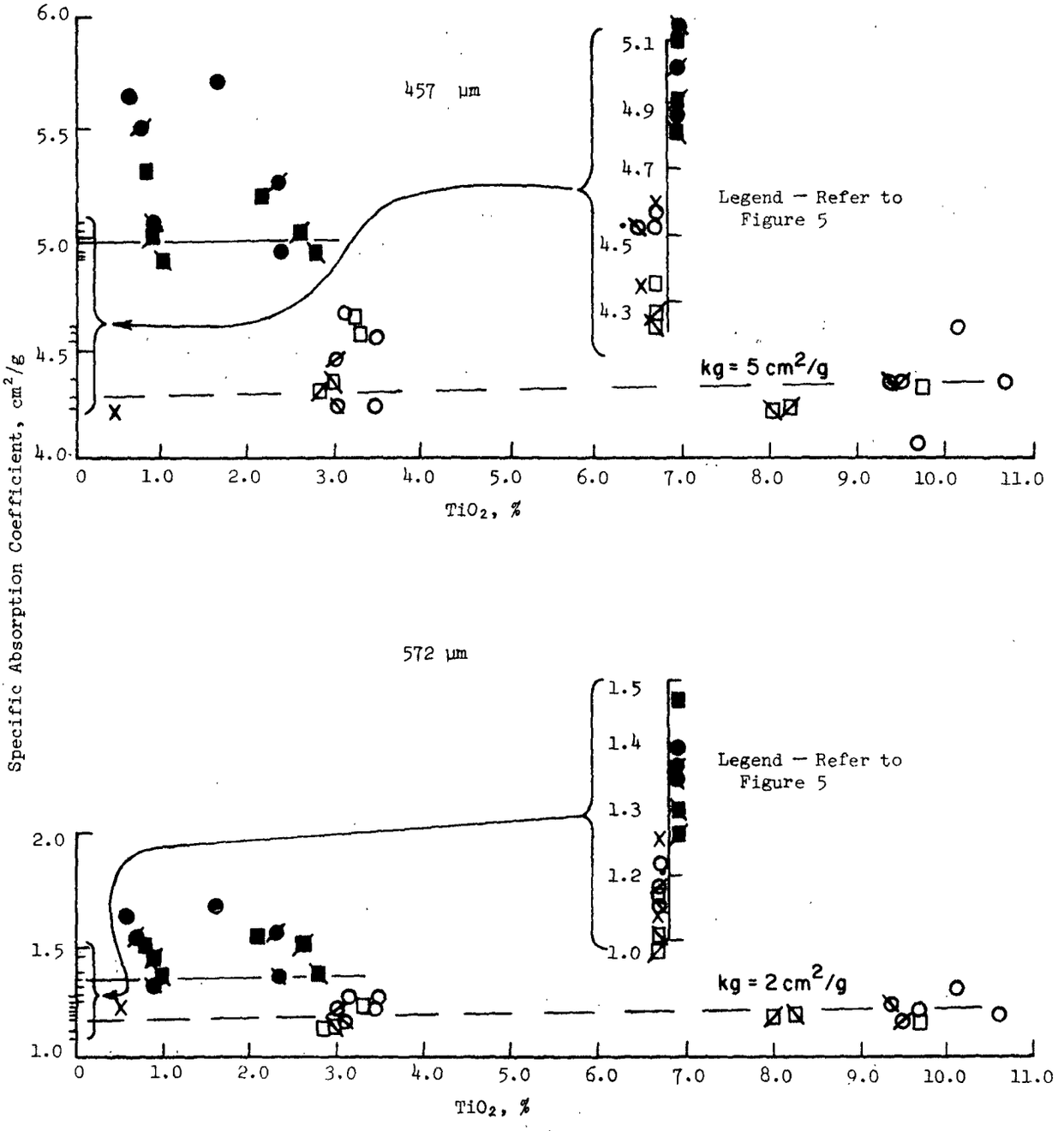


Figure 9. The Specific Scattering Absorption Coefficients vs. TiO_2 of the Paper for 445 CSF Pulp Using Light as Indicated

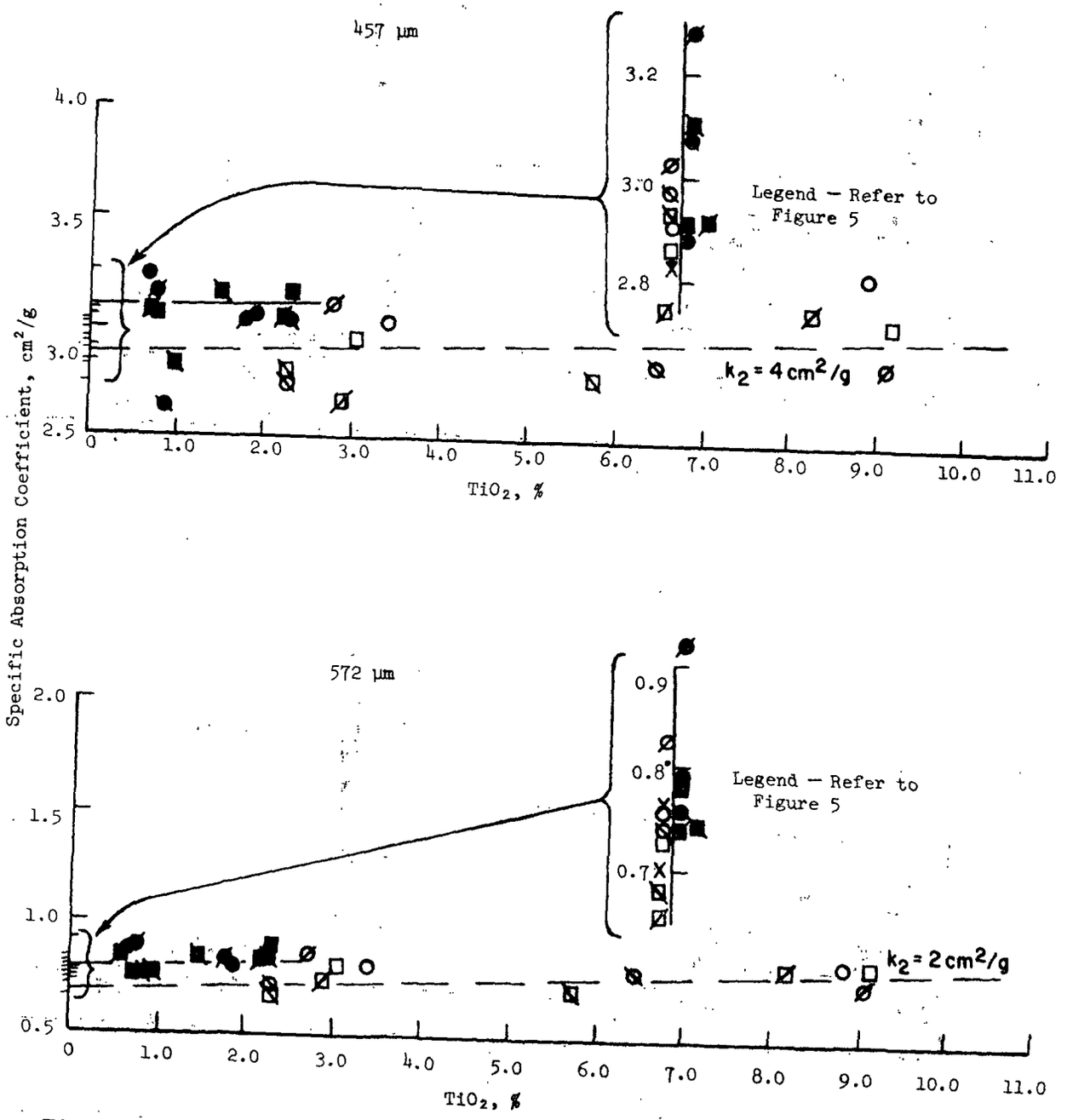


Figure 10. The Specific Absorption Coefficients vs. TiO_2 of the Paper for Classified Pulp Using Light as Indicated

CLAY

Clay Retention

The effect of alum concentration on the retention of clay, at pH 5.0, is shown in Fig. 1 for the two pulps. The very broad retention maximum occurs approximately at 10 x 10^{-5} molar alum, (2.1% based on fibers), illustrating that the retention response of each component (pulp fines, TiO_2, or clay) to alum is somewhat different. For suitable comparisons the clay studies were carried out at the same alum concentrations as used in the TiO_2 study (1 x 10^{-5} and 3 x 10^{-5} molar alum).

The retention results for both pulps are presented in Table III for the variables: clay loading (10 and 25% based on fiber); consistency (0.1 and 0.3%); agitation (70 and 140 cpm); and handsheet cycle. Most of the alum was found to be adsorbed on the fiber and clay effecting the collapse of the electric double layer. Thus, it is best to express the alum concentration on the basis of the fiber content, as in the TiO_2 study. The presence of alum is essential to retention, indicating that the sieving mechanism of retention is of minor importance in clay retention.

It is apparent from Table III that the retention is low compared to that of TiO_2, and that the retention is reduced significantly when the fines are absent. SEM examination of the handsheets shows (see Fig. 11) that the clay is primarily associated with the fines. The fiber surfaces are for the most part free of clay. In the classified pulp, the little clay that is retained is found on the few residual fines and wall attached fragments. The fact that the wall attached fibrils are devoid of clay particles, in contrast to the TiO_2 results, is probably due in part to the greater hydrodynamic shear forces on the larger platelike clay

TABLE III

THE RETENTION[a] OF FILLER CLAY BY BLEACHED KRAFT NORTHERN SOFTWOOD

	445 CSF Pulp									Classified Pulp								
Clay[b], %:	0			10			25			0			10			25		
Alum[b], %:	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0
First Cycle Handsheets																		
Consistency, %							70 cpm[c]											
0.1					22	42		20	35					9	18		6	15
0.3				6	36±2	45		29±0					4	20	18		12	
0.6						52			49						28			27
1.0						50			51						32			28
							140 cpm											
0.1					15	26		15	28					7	16		6	12
0.3					33			23						15			10	
Second Cycle Handsheets																		
							70 cpm											
0.1					32	40		24	31					9	13		7	11
0.3				8	37			34					5	20			17	
0.6						44			37						24			27
1.0						56			41						20			26
							140 cpm											
0.1					19	27		19	25					4	11		4	9
0.3					35			28						--			11±1	

[a] Defined as the percentage of the weight of filler clay in the furnish for that cycle. The level of replication is indicated where duplicate runs were made.

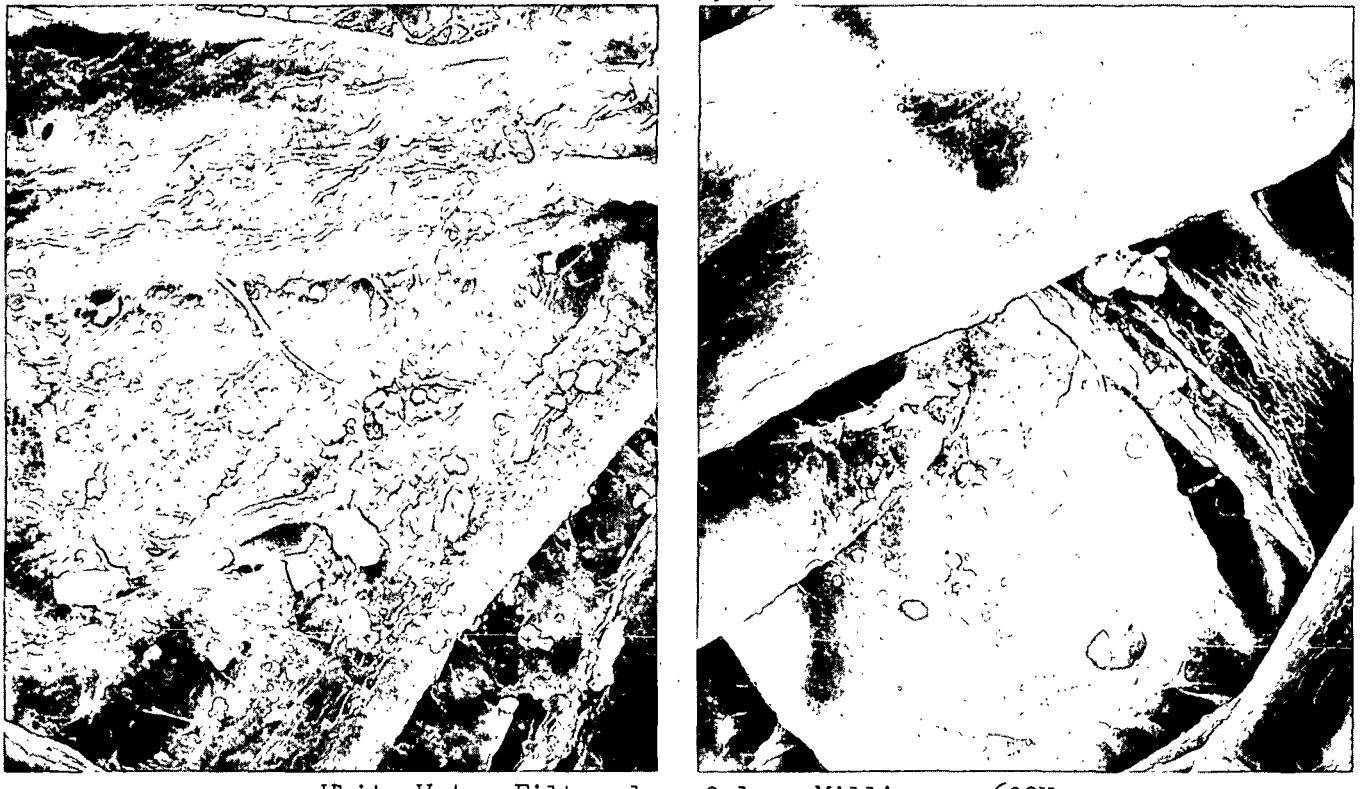
[b] Based on the OD weight of pulp.

[c] The agitator oscillates at a rate given in cycles per minute.

445 CSF

Classified

Handsheet, 1500X



White Water Filtered on 0.1 μm Millipore, 600X

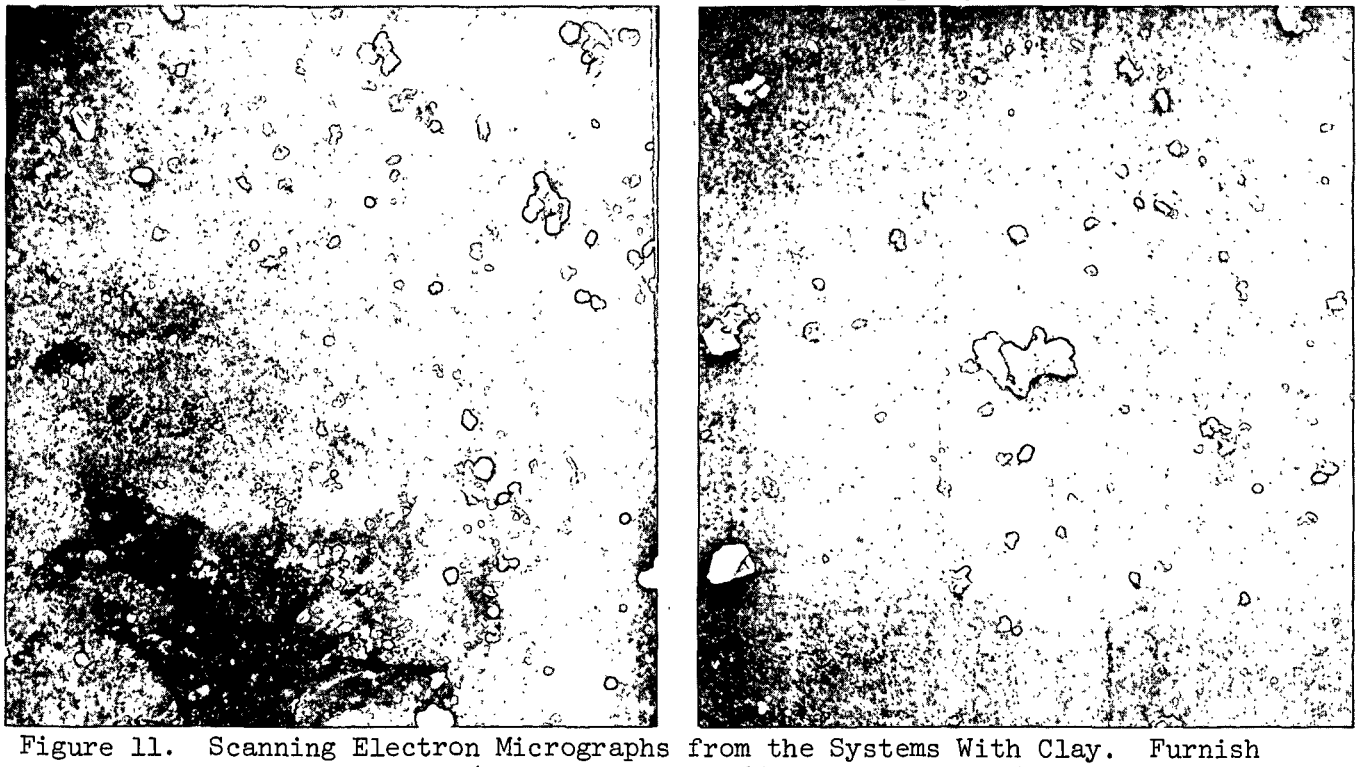


Figure 11. Scanning Electron Micrographs from the Systems With Clay. Furnish Conditions: 0.3% Consistency, 0.6% Alum, pH 5, 10% Clay, and 70 cpm

particles and possibly weaker colloidal attractive forces than those experienced by the small spherelike TiO_2 particles.

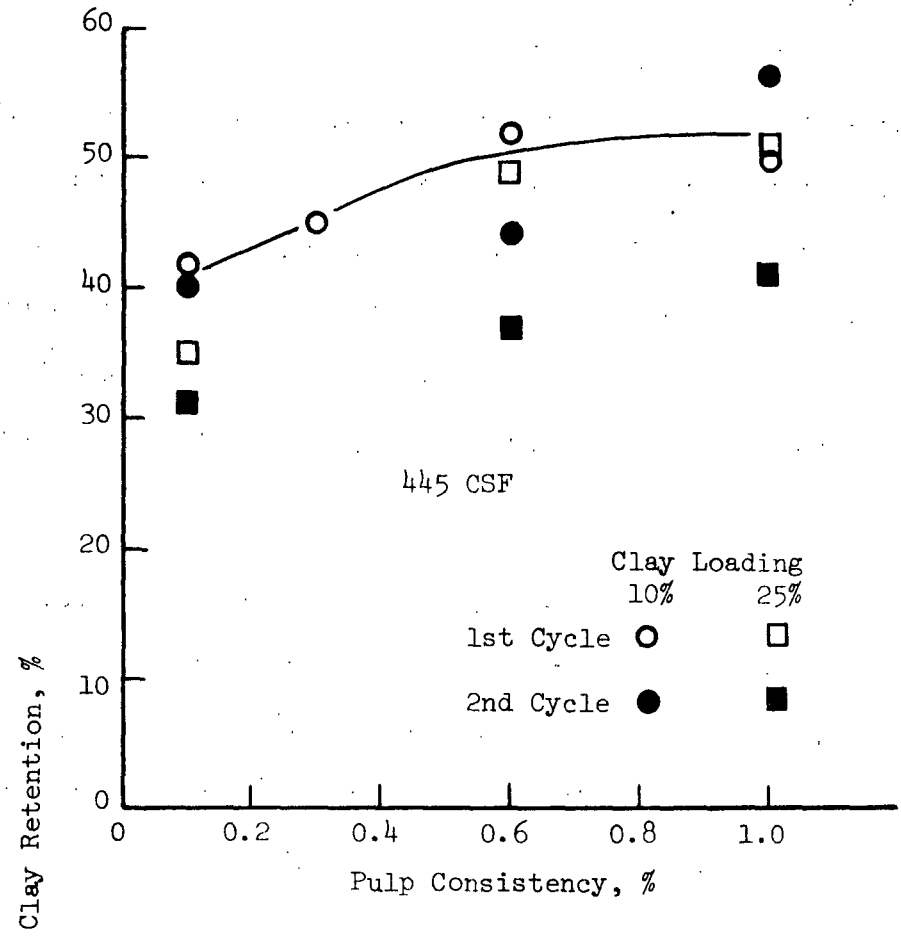
Figure 11 also shows representative micrographs of the solids in the white water. It again appears that much of the clay is associated with fines, when the latter are present. In the absence of fines, the clay forms agglomerates of relatively few particles.

The fines in the sheet serve as interfiber bridging and fiber bonding agents. Thus clay on the fines helps to fill up the interfiber gaps, thereby reducing the sheet porosity. This may be beneficial in coating and in printing. The clay, however, weakens the interfiber bonding and, as is known, dry strength agents are required to maintain strength with increased clay loading.

Both the first cycle and the second cycle retention data show essentially the same trend with the variables examined.

As noted earlier, increasing alum concentration from 0.6 to 2% generally increases the retention. The zeta potential of the material remaining in the white water (see Fig. 3 and 4) goes from anionic to cationic over this alum change for both pulps. Recalling that TiO_2, in the absence of fines, was quite cationic over this same concentration range, the retention response difference between TiO_2 and clay is apparently due to alum produced surface charge differences.

The retention also increases with consistency as shown in Fig. 12. The increase in retention above 0.6% is relatively small, indicating the minor importance again of the sieving mechanism for clay retention.



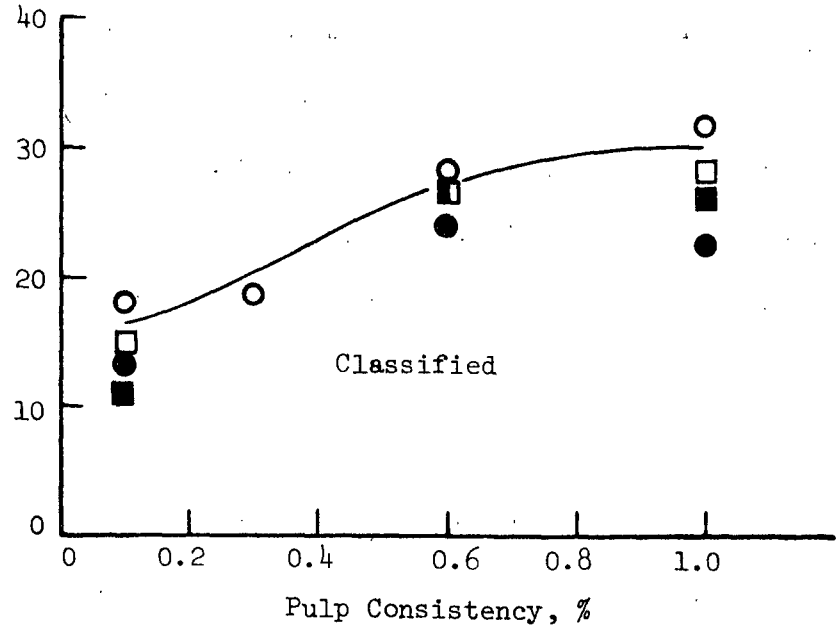


Figure 12. Clay Retention vs. Pulp Consistency with 2% Alum and Agitation of 70 cpm

The retention decreases with increased agitation for both pulps (Table III). The magnitude of the change is significantly greater than in the case of TiO_2. Since the clay is attached to the fines, any fines lost by agitation also results in clay loss. However, in the case of the classified pulp the loss must be due to the direct effect of hydrodynamic shear forces on the clay. Accordingly, significant clay losses in both pulps must occur by this route. The platelike shape of the particles which would accentuate hydrodynamic shear forces and possibly weaken fines-clay attractive forces could account for this clay sensitivity to increased agitation.

There is an indication that the retention decreases slightly with increased clay loading (Fig. 12). This may be due to a greater probability of self flocculation resulting in a larger net particle size and thus increasing the chance for loss by hydrodynamic shear. The optical data discussed later, however, indicate that the clay retained in the second cycle was better dispersed than that in the first cycle.

For both pulps the retention in the second cycle increases slightly over the first cycle retention for the 0.6% alum concentration and decreases a small amount for 2% alum (Table III and Fig. 12). Even though the zeta potential of the solids remaining in the white water does not change significantly from the first to the second cycle, the small differences observed may be due to changes in the zeta potential of the pulp, perhaps becoming more cationic with the alum addition in the second cycle.

Pulp Fines Loss

The amount of pulp fines lost during sheet making with the furnishes containing clay is listed in Table IV. These results are similar to those for

TABLE IV

PULP FINES LOST[a] IN THE FILLER CLAY CONTAINING FURNISHES OF BLEACHED KRAFT NORTHERN SOFTWOOD

Clay[a], %:	445 CSF Pulp									Classified Pulp								
	0			10			25			0			10			25		
Alum[a], %:	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0	0	0.6	2.0
First Cycle Handsheets																		
Consistency, %	70 cpm[c]																	
0.1		1.4	1.6		2.4	2.5		2.5	2.5		0.3	0.1		0.3	0.1		0.4	0.3
0.3	1.8±0.3	1.9±0.2	2.1	2.2±0.1	2.0±0.1	1.9		2.0	--	0.2±0.0	0.4	0.3	0.4	0.4	0.5		0.5	--
0.6						1.5			1.3						0.2			0.3
1.0						1.2			1.4						0.1			0.2
	140 cpm																	
0.1		2.2	2.1		2.6	--		2.6	2.8		0.2	0.2		0.2	0.2		0.3	0.2
0.3	1.9				3.0			1.8		0.1	0.2		0.6	0.5			0.3	
Second Cycle Handsheets																		
	70 cpm																	
0.1		2.6	2.8		3.1	3.3		2.7	3.8		0.2	0.1		0.3	0.3		0.2	0.1
0.3			2.3	2.6	2.1±0.2	--		2.4	--		0.3	0.2		0.6	--		0.5	--
0.6						2.0			1.8						0.3			0.4
1.0						1.5			1.6						0.3			0.3
	140 cpm																	
0.1		2.7	2.9		3.5	4.2		3.4	3.2		0.2	0.1		0.4	0.2		0.5	0.2
0.3					3.0			2.9			0.2			0.6			0.5	

[a] Given as the percentage of the OD weight of the pulp in the furnish. The level of replication is indicated where duplicate runs were made.
[b] Based on the OD weight of pulp.
[c] The agitator oscillates at a rate given in cycles per minute.

the TiO_2 containing furnishes (Table II). Thus, the type of filler presumably has little influence on the mechanism(s) of fines loss. The loss increases slightly with increased agitation and decreases with increased consistency. However, there is no apparent change in the loss with increased clay loading, in contrast to the slight increase observed with TiO_2, particularly in the classified pulp. Again, this result is probably due to differences in the electrokinetic properties of the clay vs. the TiO_2. The latter are much more cationic under similar conditions and thus heavily loaded fines would be expected to behave cationically.

Optical Properties

Presented in Fig. 13, 14, 15, and 16 are the light scattering coefficients of the handsheet sets listed in Table III vs. the sheet clay content. The expected linear relationships are masked to some extent by the apparent scatter in the data. The latter is believed to be caused mainly by the changes in the alum and consistency conditions under which the handsheets were made. Note that the data with common consistency and alum concentration show less scatter from linearity. The linear functions have similar slopes but different intercepts. This suggests that the scattering coefficient of the clay is constant but the scattering coefficient of the pulp changes with consistency and alum concentration. Again this could be an electrokinetic affect. The estimated average line is indicated. The values of the scattering coefficients are good to excellent as compared to reported values for clay (28-30). The lower scattering coefficients for the clay with the classified pulp compared with those with the 445 CSF pulp indicates that the average particle size of the former is larger. This indicates that some self coagulation has occurred, in the absence of fines. The scattering coefficients of the clay in the second cycle handsheets are equal or greater than those from

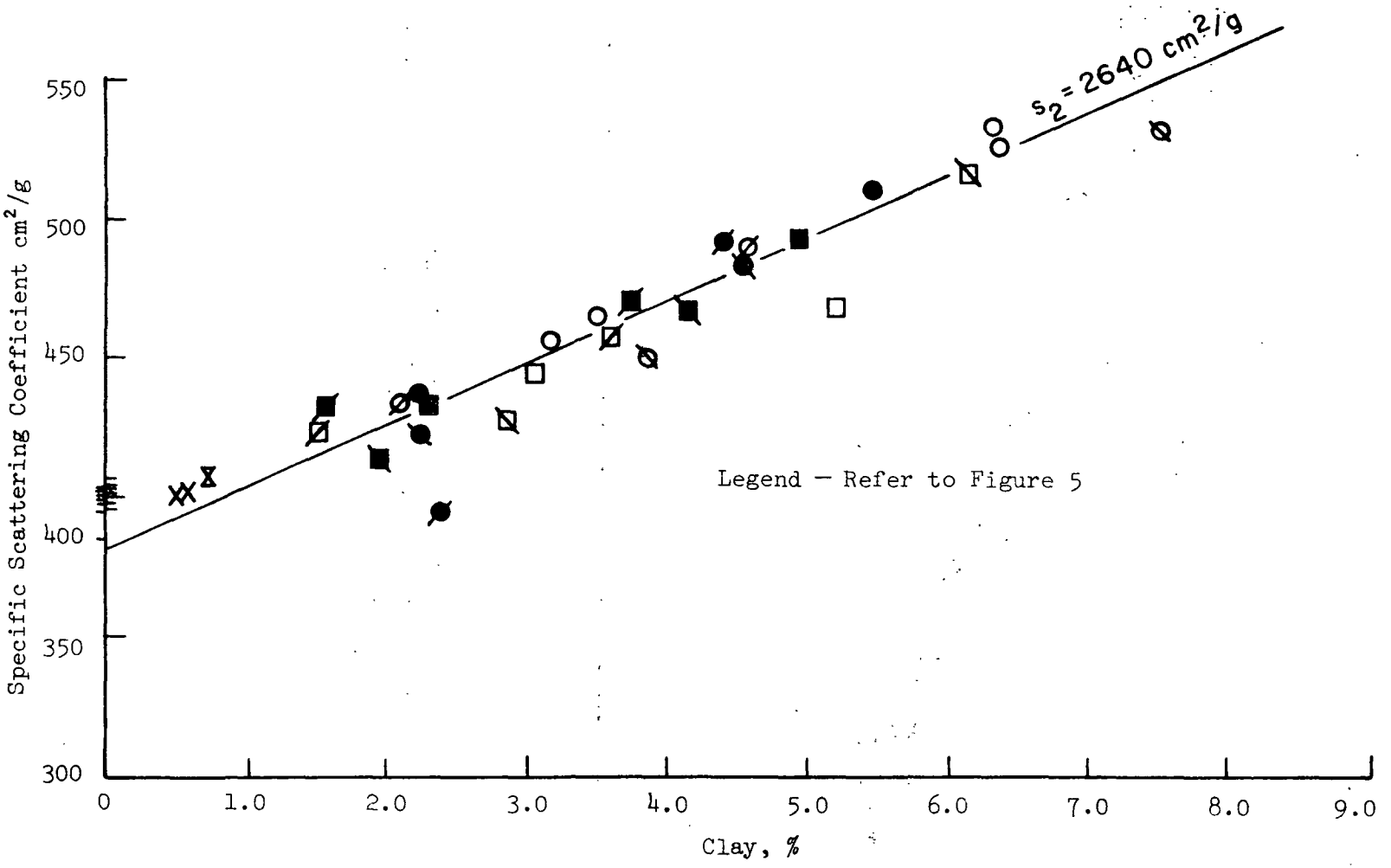


Figure 13. The Specific Scattering Coefficients vs. Clay Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 457 µm. See Figure 5 for Scattering Values for Zero TiO_2 or Clay Content

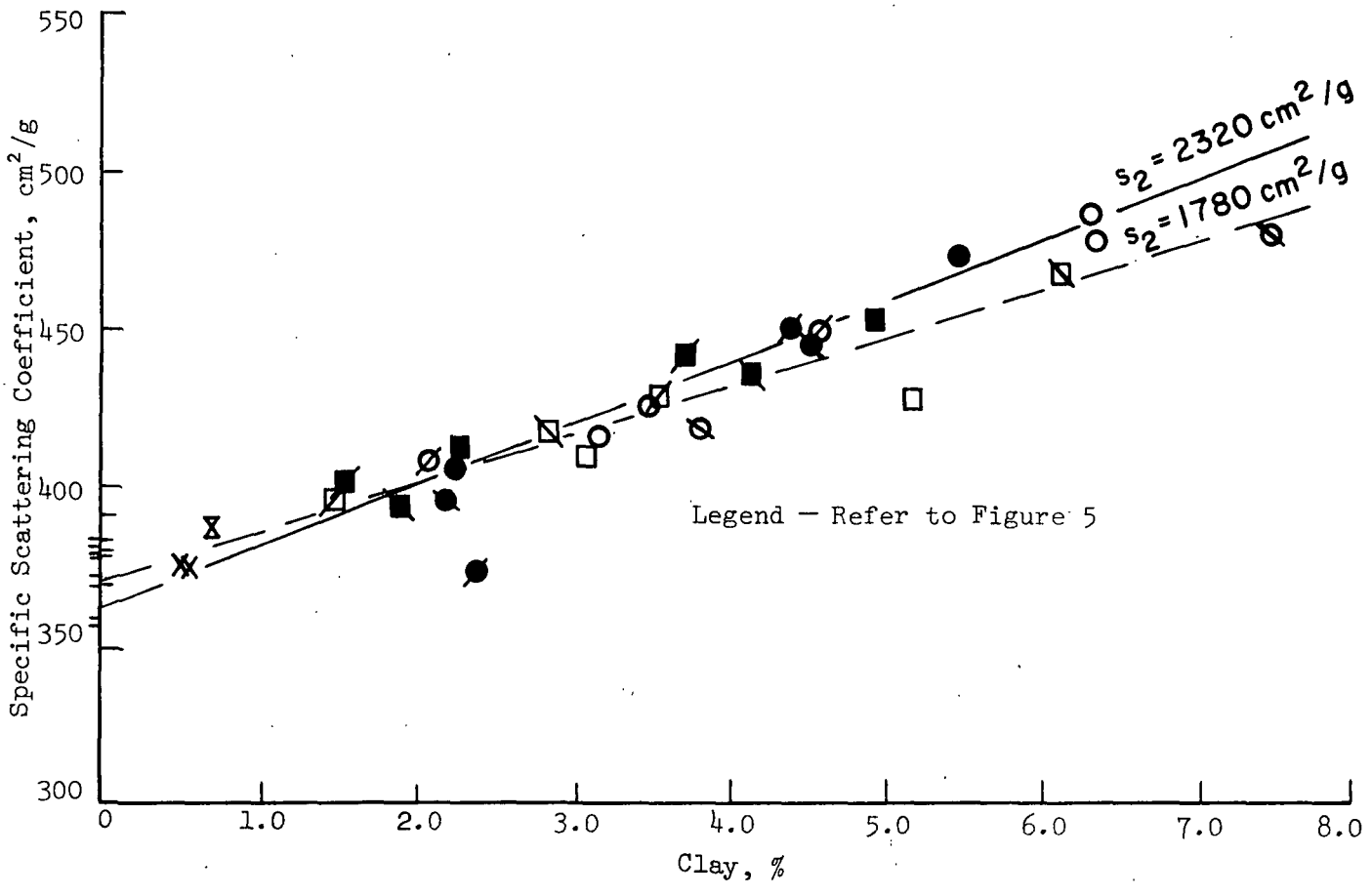


Figure 14. The Specific Scattering Coefficients vs. Clay Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 572 μm. See Figure 6 for Scattering Values for Zero TiO_2 or Clay Content

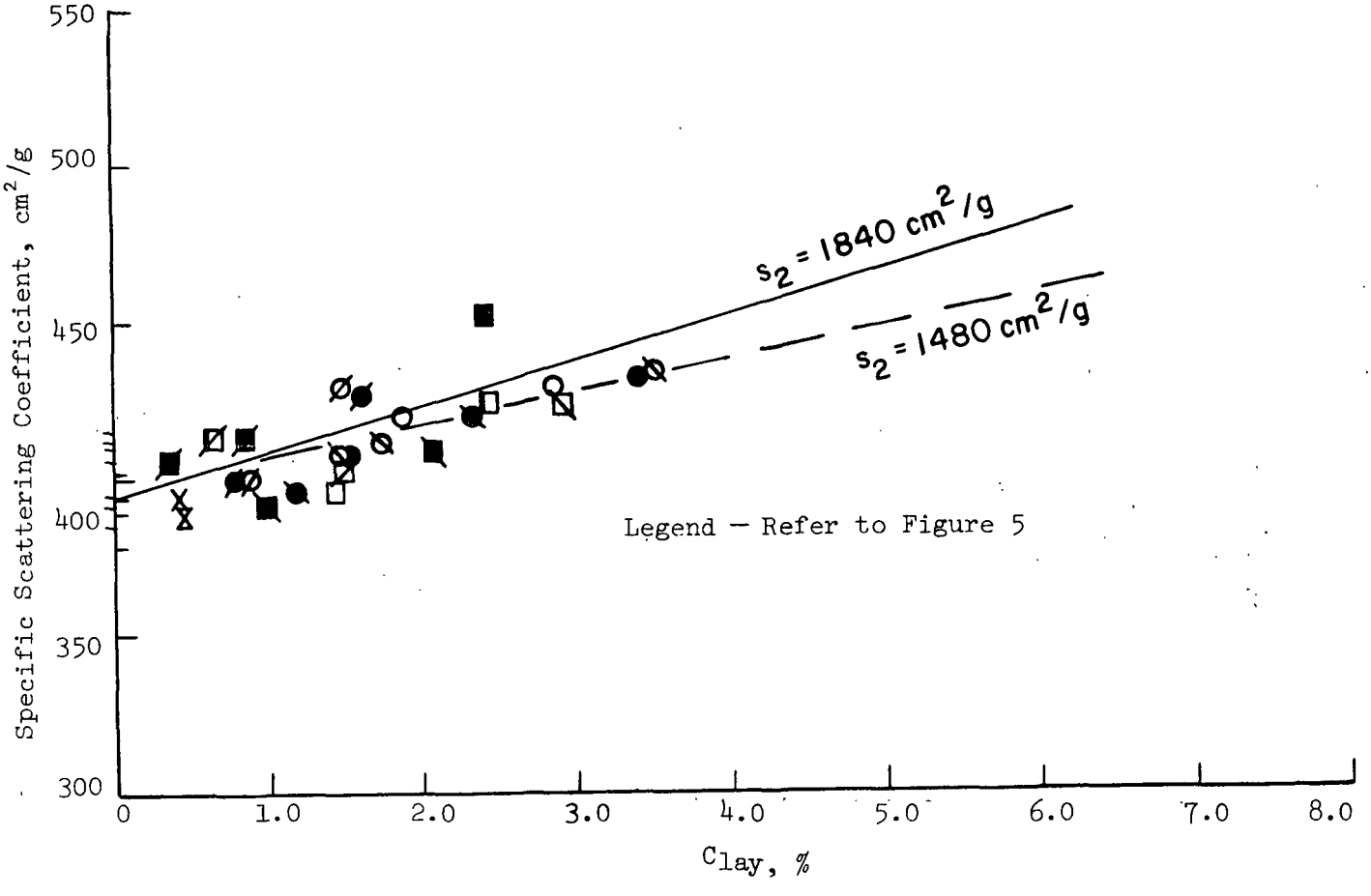


Figure 15. The Specific Scattering Coefficients vs. Clay Content of the Paper for Classified Pulp Using Light of Wavelength, 457 μm. See Figure 7 for Scattering Values for Zero TiO_2 or Clay Content

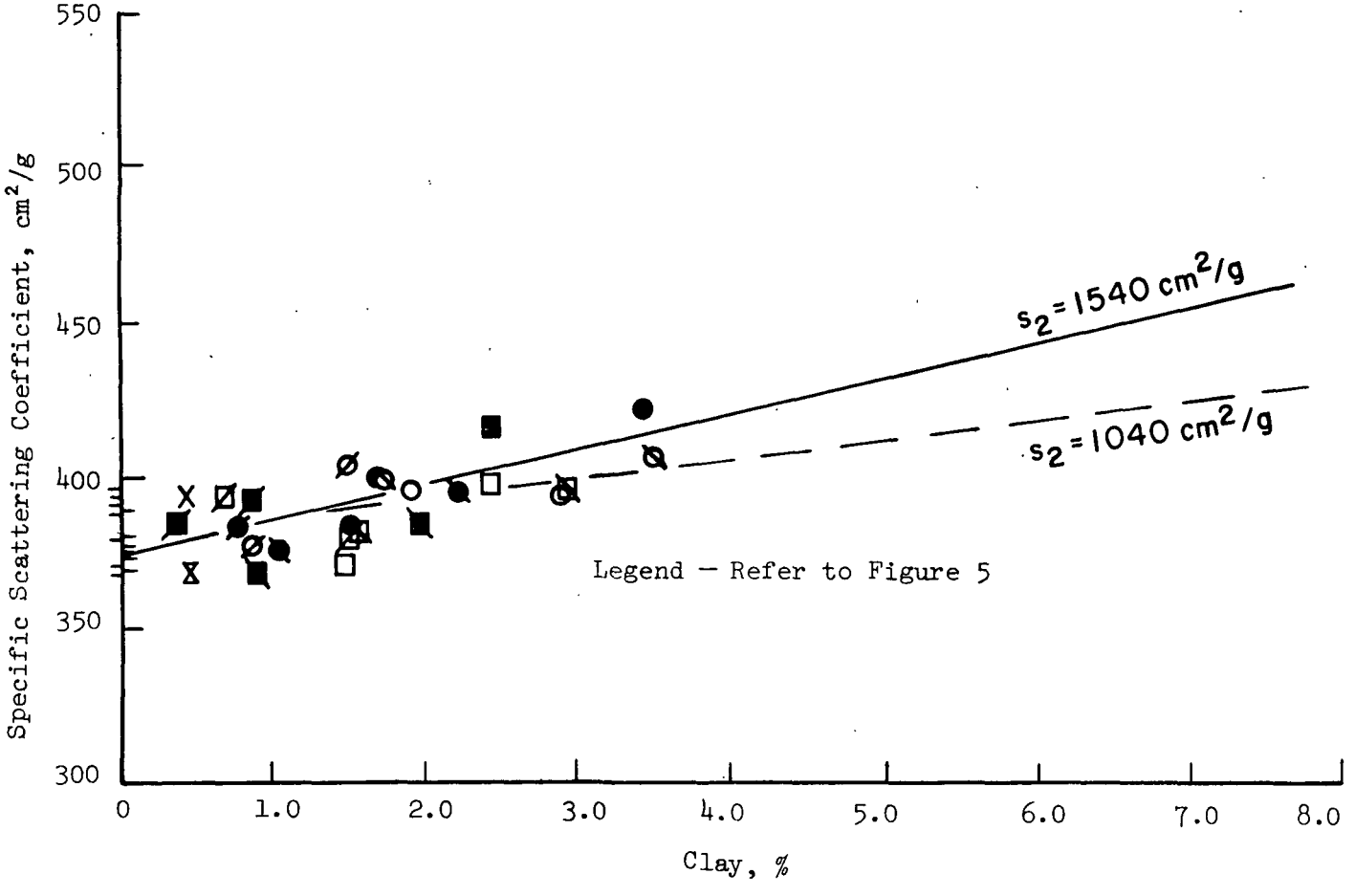


Figure 16. The Specific Scattering Coefficients vs. Clay Content of the Paper for Classified Pulp Using Light of Wavelength, 572 μm. See Figure 8 for Scattering Values for Zero TiO_2 or Clay Content

the first cycle. This suggests that some self flocculation occurs at high filler concentrations in the first cycle. The effect is larger when the fines are absent (as with TiO_2). The high specific scattering coefficients of the clay in the handsheets of the second cycle indicate that a favorably small average particle size of retained clay is achieved. However, the scanning electron micrographs of the clay in the white water (Fig. 11) show that much of this white water-recycled clay is coagulated with the fines (when present) or with itself. Accordingly the coagulation forces must be weak compared with the hydrodynamic shear forces produced in the subsequent sheet making process.

Presented in Fig. 17, 18, 19, and 20 are the specific absorption coefficients of the handsheets vs. the clay content. The data consists of sets at constant consistency and alum concentration giving lines of common slope but different intercepts. Estimated best lines are drawn for the first handsheet data, and the second handsheet data when appropriate. In some instances the value of the intercept does not agree with the measured k of the pulp. The specific absorption coefficients of the retained clay are of the same magnitude as those reported in the literature (29), increasing with an increase in the wavelength. The recycled clay has essentially the same values as the initially retained clay.

ALUM

The fate of the aluminum and sulfate ions added to the furnish is of importance in the retention process. These ions have a significant role in effecting flocculation by the compression and/or collapse of the electric double layers of the furnish components. Since alum is added at each cycle (comparable to continuous addition on a machine system) the amount remaining in the white water can influence the effectiveness of the next addition. This is one of the

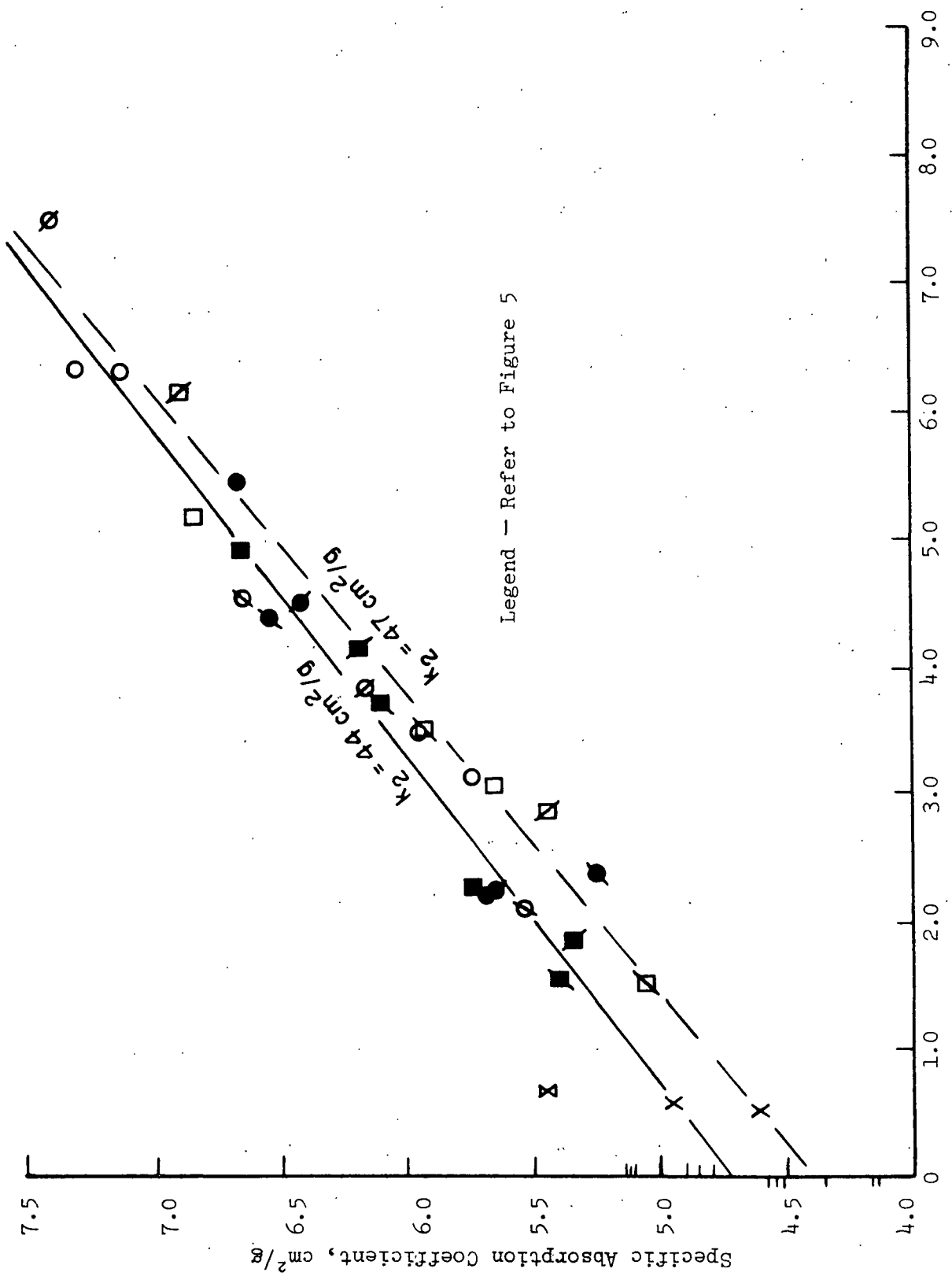


Figure 17. The Specific Absorption Coefficients vs. Clay Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 457 µm. See Figure 9 for Absorption Values for Zero TiO_2 or Clay Content

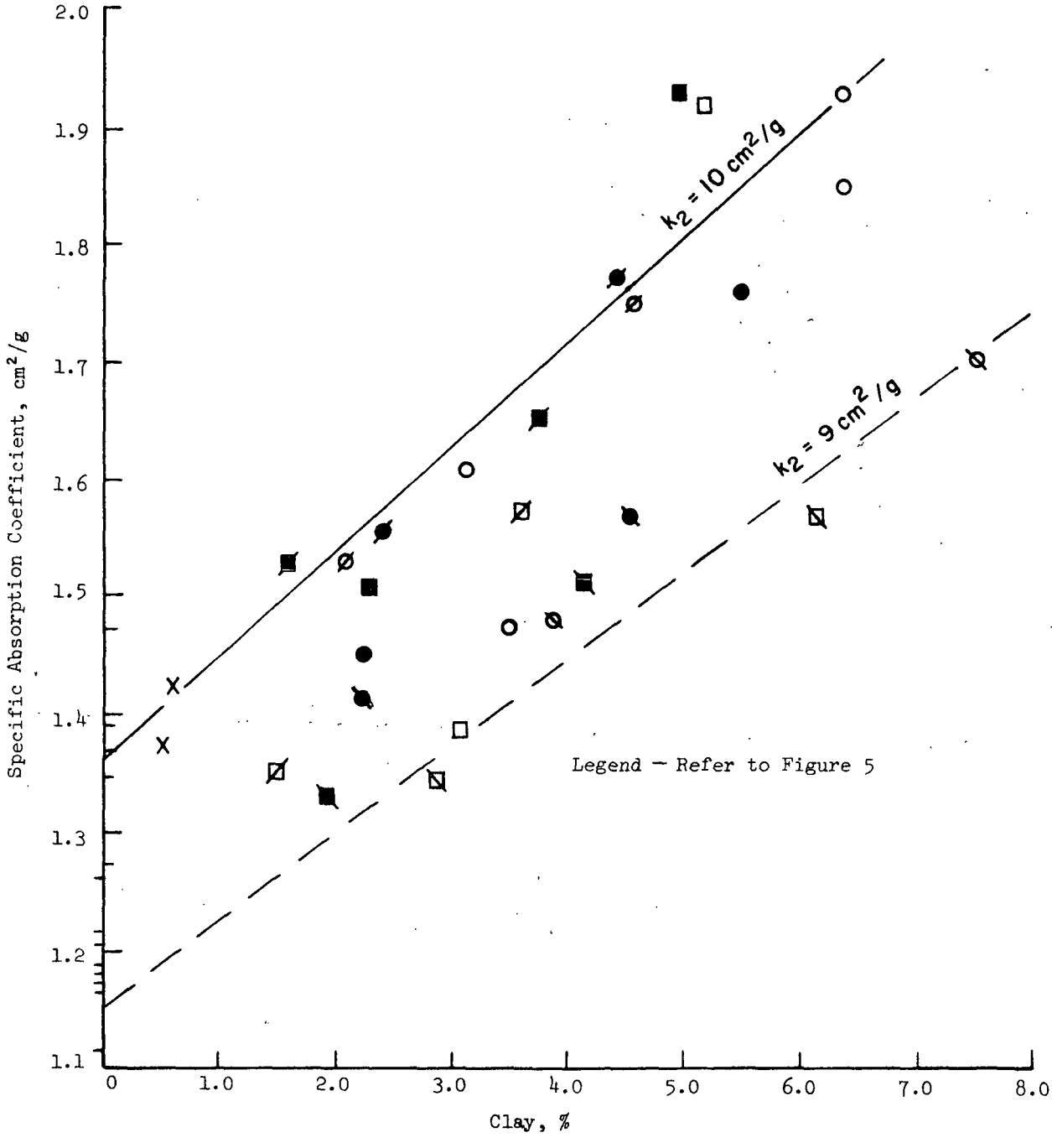


Figure 18. The Specific Absorption Coefficients vs. Clay Content of the Paper for 445 CSF Pulp Using Light of Wavelength, 572 µm. See Figure 9 for Absorption Values for Zero TiO_2 or Clay Content

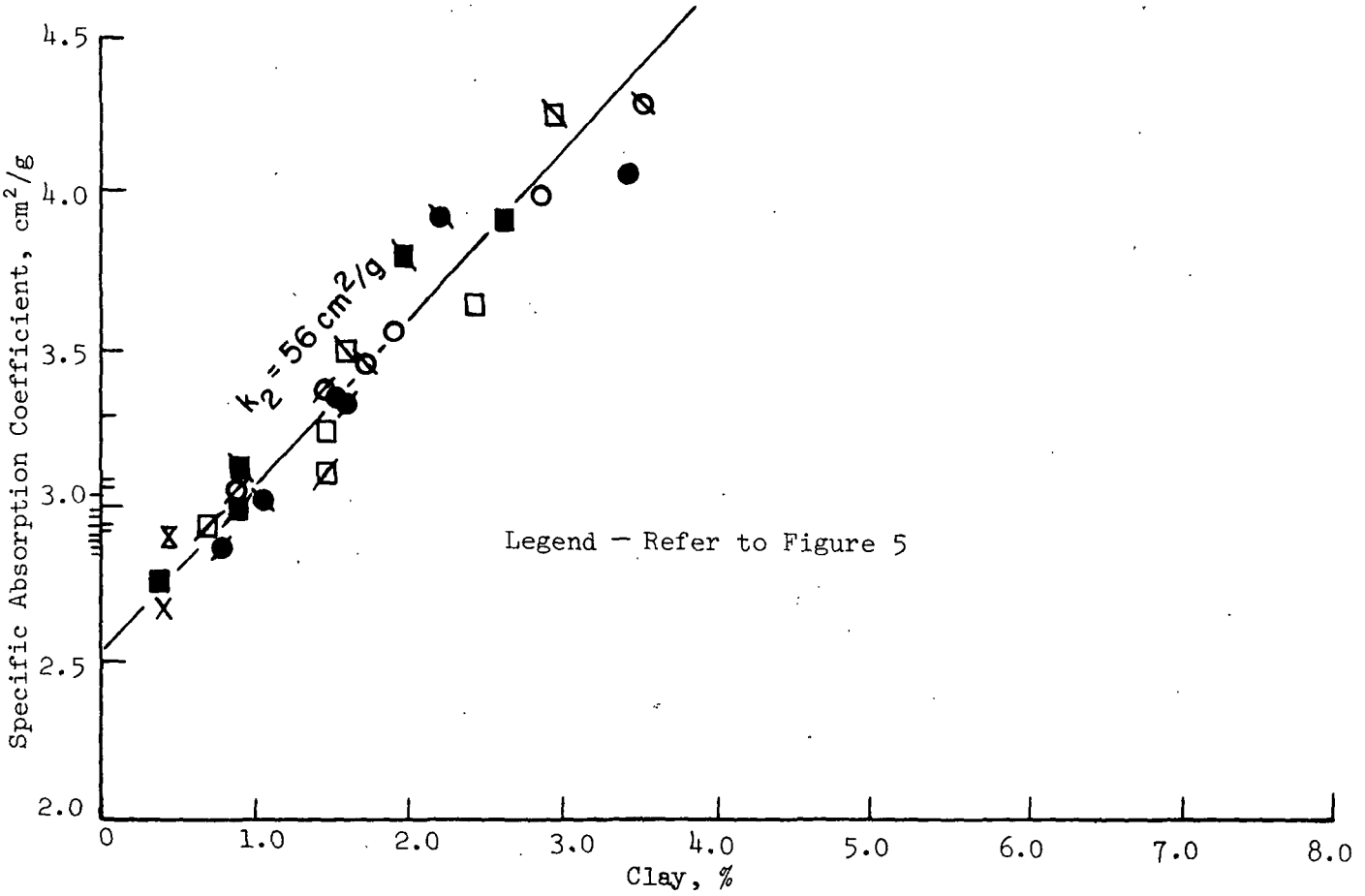


Figure 19. The Specific Absorption Coefficients vs. Clay Content of the Paper for Classified Pulp Using Light of Wavelength, 457 μm. See Figure 10 for Absorption Values for Zero TiO_2 or Clay Content

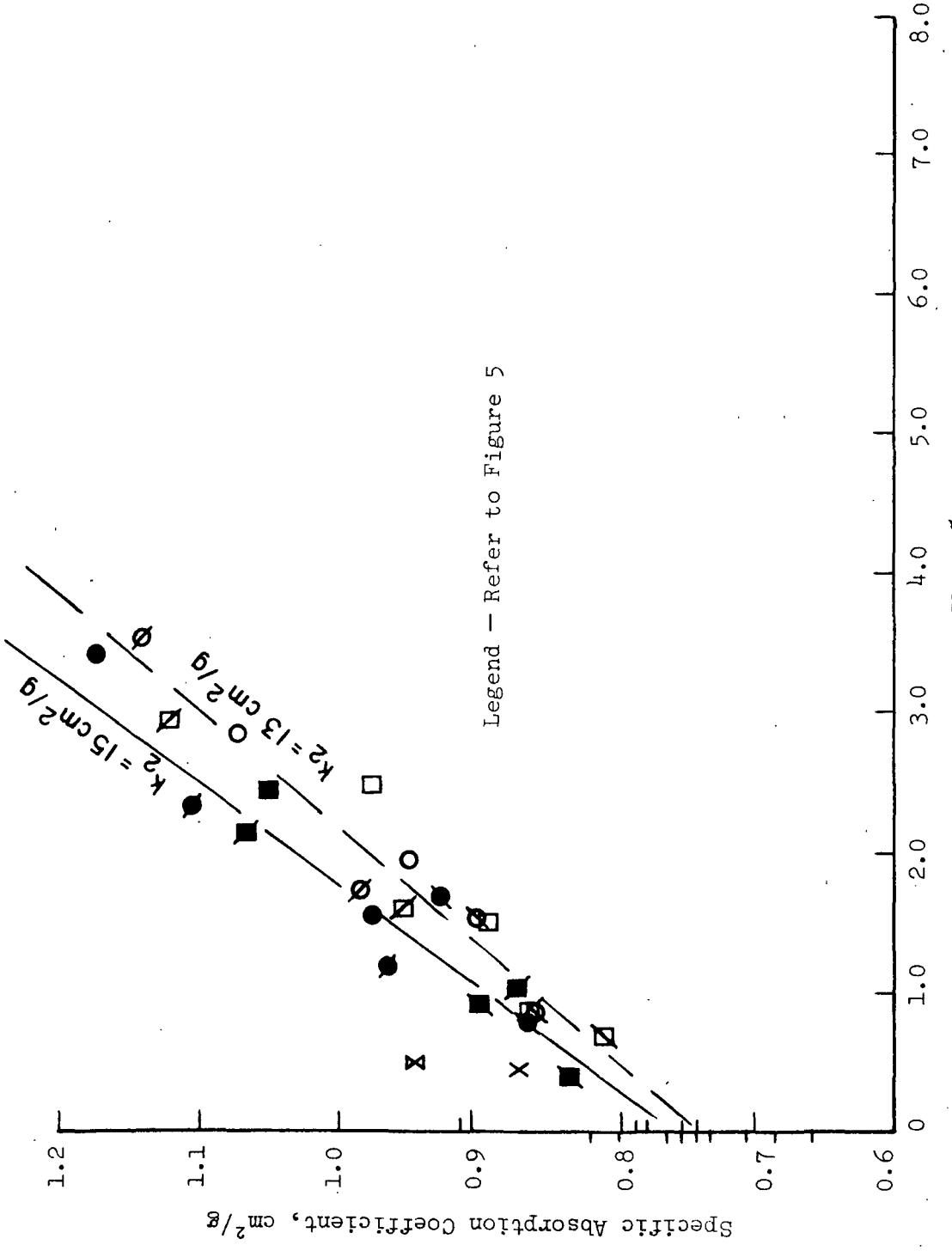


Figure 20. The Specific Absorption Coefficients vs. Clay Content of the Paper for Classified Pulp Using Light of Wavelength, 572 µm. See Figure 10 for Absorption Values for Zero TiO_2 or Clay Content

particular concerns of the next phase of the project. However, it is felt that summarizing the results of the systems reported herein contributes to the understanding of these systems.

Presented in Fig. 21 are the average results of the amount of aluminum or sulfate adsorbed by the furnish components, based on the amount added to the furnish in that particular cycle (i.e., the amount carried over from the first cycle is not included in the percentage calculations). The data are listed in Tables XV, XVI, XVII and XVIII in Appendix I.

The amount of aluminum ion adsorbed increases greatly when the consistency is increased from 0.1 to 0.3%, becoming at least 90% at the latter consistency. Since it is the hydrolyzed species of aluminum which are adsorbed, the higher alum concentration at the fixed pH 5 produces the greater percentage change. There is only small effect on these adsorption results by the type of pulp (in this study the difference in the pulps is essentially due to differences in specific area), the filler type, and the loading (again probably an area effect). The cycle has essentially no effect, which is probably due to the dominance of the pulp rather than recycled material on adsorption sites. Thus very little of the aluminum ion is recycled and no serious effects on retention by aluminum ion build up are expected. This finding is consistent with the data on machine systems reported by Brecht et al. (12,13) and Aldrich and Janes (21).

The sulfate adsorption is high at 0.1% consistency, as little or no alkali is needed to adjust pH, and the sulfate adsorbs as the counterion for the adsorbed hydrolyzed aluminum ion. At the higher consistency and/or the second cycle enough alkali is added so that the adsorbed hydrolyzed aluminum ion needs little sulfate counterion and essentially no SO_4^{-2} is adsorbed. Again these results

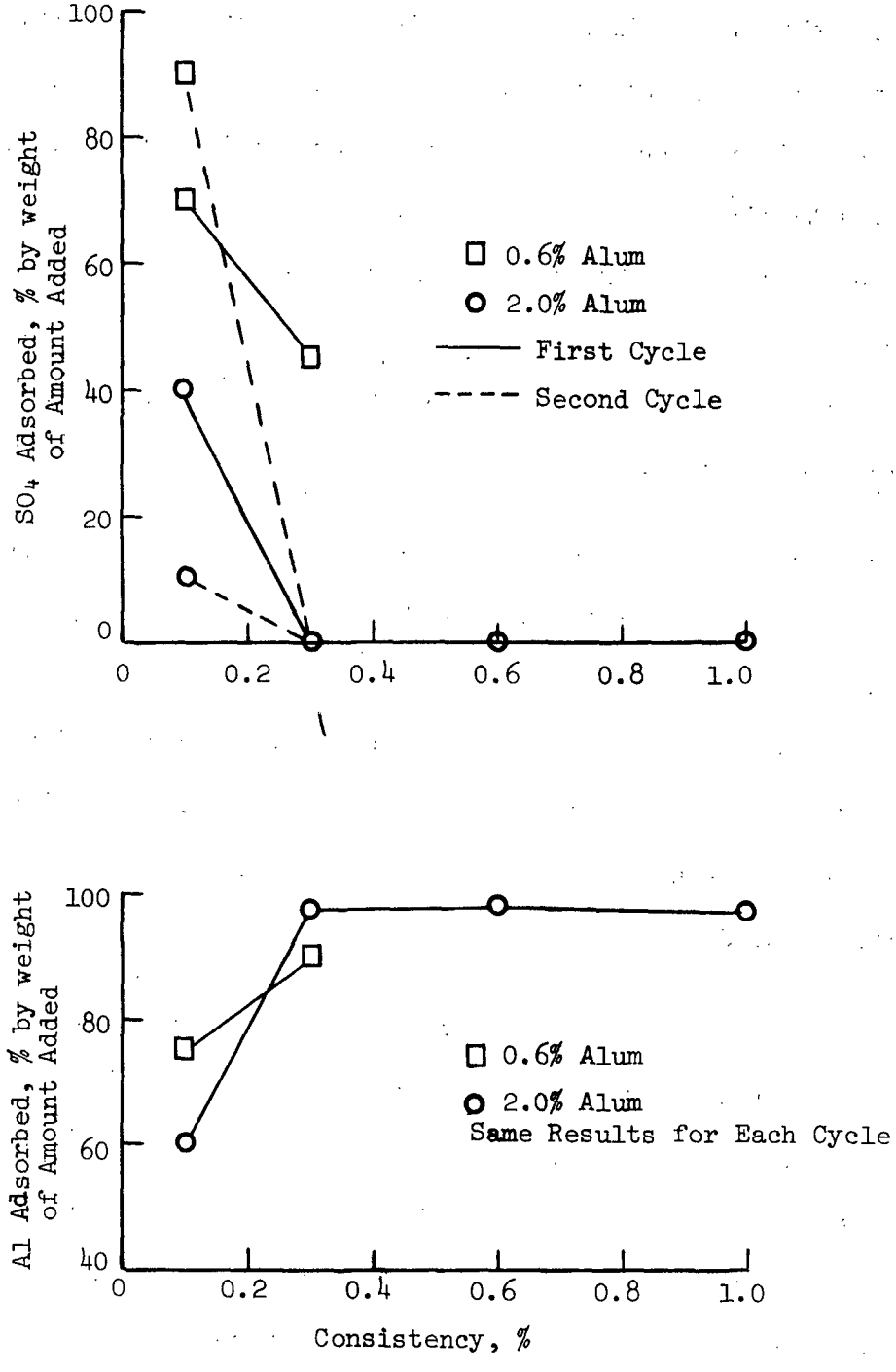


Figure 21. The Amount of the Ions from Alum Adsorbed by the Furnish Components at pH 5

vary slightly with the pulp, filler, and loading. In addition to this, some sulfate may be brought in by the kraft pulp. Virtually all of the sulfate remains in the white water and this could cause retention and sizing problems as it builds up by complexing with added alum (32). The fact that sulfate is adsorbed under some low alum concentration conditions is consistent with the work of Aldrich and Janes (21). They found no sulfate build up in their closed run with low alum and resin concentrations, as opposed to continuous sulfate build up at higher concentrations in their other two runs.

The distribution and form of the alum on the filler, fines and fiber cannot be fully controlled, in spite of the control of alum, consistency and initial loading, and pH. The small shifts in retention and optical properties with consistency, alum concentration, loading, pulp, and cycle are due mainly to changes in the effective surface charge. Although the zeta potential of the suspended particles was determined, the state of the fibers and of the filler retained was not measured.

Because there were some brass parts in the sheet mold which contacted the furnish and white water, the amount of copper ion introduced was of concern as it could affect the colloidal behavior of the control system (i.e., system with no alum). It was found that the amount of Cu^{+2} was always less than 1 ppm and it was introduced by the pulp rather than the equipment. It was, thus, of no concern. The data are listed in Table XIX and XX in Appendix I.

CONCLUSIONS

Good retention of TiO_2 in bleached kraft northern softwood pulp with alum is not dependent on the presence of "free" pulp fines since the fibrils protruding from the walls of the fibers provide ample sites for pigment attachment. In contrast to this, the retention of clay is quite dependent on the presence of fines and only a relatively small amount of clay is retained by protruding fibrils. Since the clay retention is significantly reduced by increased agitation, regardless of the presence of fines, the hydrodynamic shear forces of mixing and drainage cause most of the clay loss by direct effect rather than through loss with fines. If protruding fibrils are thought of as pulp fines still attached to the fiber, then both titanium dioxide and clay are retained through interactiion with pulp fines. This interaction is very sensitive to the surface chemical forces (which in this study were established by alum concentration at pH 5), consistency, cycle, and filler loading, in that order of importance. The platelike clay particles, however, do not remain on the protruding fibrils because they experience greater hydrodynamic shearing forces from mixing and drainage, and perhaps weaker surface chemical forces, than the smaller spherelike titanium dioxide particles.

The good to excellent specific scattering coefficients of both TiO_2 and clay in the first cycle handsheet are improved by the presence of pulp fines, indicating that the latter reduce the extent of self flocculation in this initial cycle. The excellent specific scattering coefficients of the fillers retained in the second cycle implies that the filler-fines agglomerates and filler self-agglomerates in the initial white water were weak enough to be redispersed during the subsequent recycle.

The recycled fines increase the specific adsorption coefficients of the pulp in the subsequent handsheet, while the specific scattering coefficients are constant. This loss in whiteness may be caused by the build up in the white water and ultimate retention of residual lignin in the fines.

FUTURE WORK

The next objective sought in the project is to identify causes of retention loss. Systems with recycled white water, of a type approaching that found in mills, will be used. The particular concern will be the effects of ion concentration changes, and the build up of pulp source components, on the retention of fillers and pulp fines, in furnishes using very hard water recycled many times. A prepared hard water (e.g., 500 ppm hardness) containing Ca^{+2}, Mg^{+2}, HCO_3^-, SO_4^{-2}, and Cl^- will be used. Changes will be defined with respect to Cl^- as this ion is least adsorbable. The ion of particular concern is SO_4^{-2} as this will be changing with alum addition and can complex with the aluminum ions. The recycle process will be carried out for up to ten cycles, or perhaps more if needed.

The significant decrease in TiO_2 retention upon recycle needs further examination. The possibility of a "retention inert" fraction of TiO_2 will be examined by a repeated recycle approach.

In order to broaden the base of understanding of the role of fines on retention, a bleached kraft northern hardwood pulp and a stone groundwood pulp of northern softwood will be tested under selected conditions for retention, optical behavior, and location in the handsheet and white water. Comparisons will be made with the results on the bleached kraft softwood pulp reported here.

EXPERIMENTAL

MATERIALS

Pulp

A bleached kraft northern softwood pulp was chosen for this work because of the good sheet forming quality of these thin walled fibers. This was necessary because handsheets had to be made at consistencies approaching those used in commercial furnishes and with good enough formation for valid optical measurements. The fiber species in the pulp were principally spruce and/or hemlock with smaller percentages of true fir, larch, hard pine (probably a species of jack pine), and a trace of white pine.

A moderately refined fines-pulp was prepared by beating two 5 lb batches of the above pulp in a 5-lb capacity Valley beater at 2.25% consistency in tap water with a bed plate load of 36 lb for 48-50 minutes to a freeness of 445 cc CSF. The combined pulp was dewatered by centrifugation. It was then washed twice with deionized water by resuspending at about 5% consistency using a pulp shredder and dewatering. After the final dewatering, formalin was mixed thoroughly with the pulp (25% solids) to give a final concentration of 1% based on dry fiber, and the pulp was stored in plastic bags in a cold room. This pulp is designated 445 CSF.

The no-fines pulp was prepared by slushing two 5-lb batches of pulp in the Valley beater at 2.25% consistency with no bed plate load for 15 minutes. The fines were removed by classifying the dispersed pulp on the IPC Web Former in the following manner. The slushed pulp was diluted to 1% in the stock chest and diluted again to the maximum (0.03%) before flowing out on the wire. [Filtered tap water was used.] The wire (48 x 72 mesh) was run at maximum speed (50 fpm). The wet mat was doctored off the drying can (at room temperature) and put through this classification

a second time. Formalin was added to final wet mat (31% solids) and it was stored in plastic bags in the cold room. This pulp is designated classified.

The fiber length distribution of the two pulps is given in Table V. As expected, the 445 CSF pulp has a significantly higher frequency in the shorter lengths which are probably fiber segments. The pulp fines are not truly revealed in these data as they would be much smaller than 0.1 mm. Figure 22 shows SEM micrographs of the suspended solids (filtered on 0.1 μm average pore size Millipore filters) in the white water from handsheet preparations with the pulp only. The very thin "flakes" of material (appearing as dark blotches) were commonly observed in the 445 CSF pulp and under much higher magnification (e.g., 2000X) fibrils of a variety of sizes are seen. The amounts of soluble organics released by these pulps when dispersed in water are presented in Table VI. These values were determined by carbon analysis of the water obtained by filtering the white water through a 0.1 μm Millipore filter. The classified pulp still has about 60% of the soluble organics that occur in the 445 CSF pulp. As expected, the amount of solubles increased about the same with each cycle, increased with consistency, decreased with increasing alum concentration, and was independent of agitation. At 0.3% consistency, 12 ppm is equivalent to about 0.4% of OD weight of the fiber, assuming that the CO_2 weight is equal to an equivalent pulp weight.

Listed in Table VII are the chemical and hydrodynamic properties of the pulp. The carbohydrate content of the two is essentially the same, as expected, indicating that the pulps have a common hemicellulose type, amount, and distribution in the pulp. The lignin content was too low for the method to discern any difference in the pulps. Both the extractives and the ash decrease significantly with the removal of fines, which is the result usually found. Finally, as expected, the beaten fiber has a much higher hydrodynamic surface area and swollen volume.

TABLE V

FIBER LENGTH DISTRIBUTION

Interval, mm	445 CSF Frequency, %	Classified Frequency, %
0.0-0.1	0.0	0.0
0.1-0.3	8.2	1.1
0.3-0.5	19.9	6.4
0.5-0.7	15.4	6.9
0.7-0.9	12.6	7.1
0.9-1.1	8.6	8.4
1.1-1.3	7.3	7.6
1.3-1.5	4.5	8.5
1.5-1.7	5.1	8.0
1.7-1.9	3.3	7.6
1.9-2.1	2.6	7.6
2.1-2.3	2.4	5.8
2.3-2.5	2.4	6.0
2.5-2.7	1.8	5.3
2.7-2.9	1.6	3.9
2.9-3.1	1.8	3.0
3.1-3.3	1.1	2.6
3.3-3.5	0.5	1.9
3.5-3.7	0.4	0.8
3.7-3.9	0.3	0.5
3.9-4.1	0.2	0.6
4.1-4.3	0.1	0.3
4.3-4.5	0.0	0.1
4.5-4.7	0.0	0.1
4.7-4.9	0.1	0.1
4.9-5.1	0.0	0.1
5.1-5.3	0.0	0.0
5.3-5.5	0.0	0.1
	100.2	100.4
Total Fibers Meas.	1471	1443
Arith. Av. Length	1.07 mm	1.71 mm
Weighted Av. Length	1.68 mm	2.17 mm
Second Weighted Av. Length	2.24 mm	2.54 mm

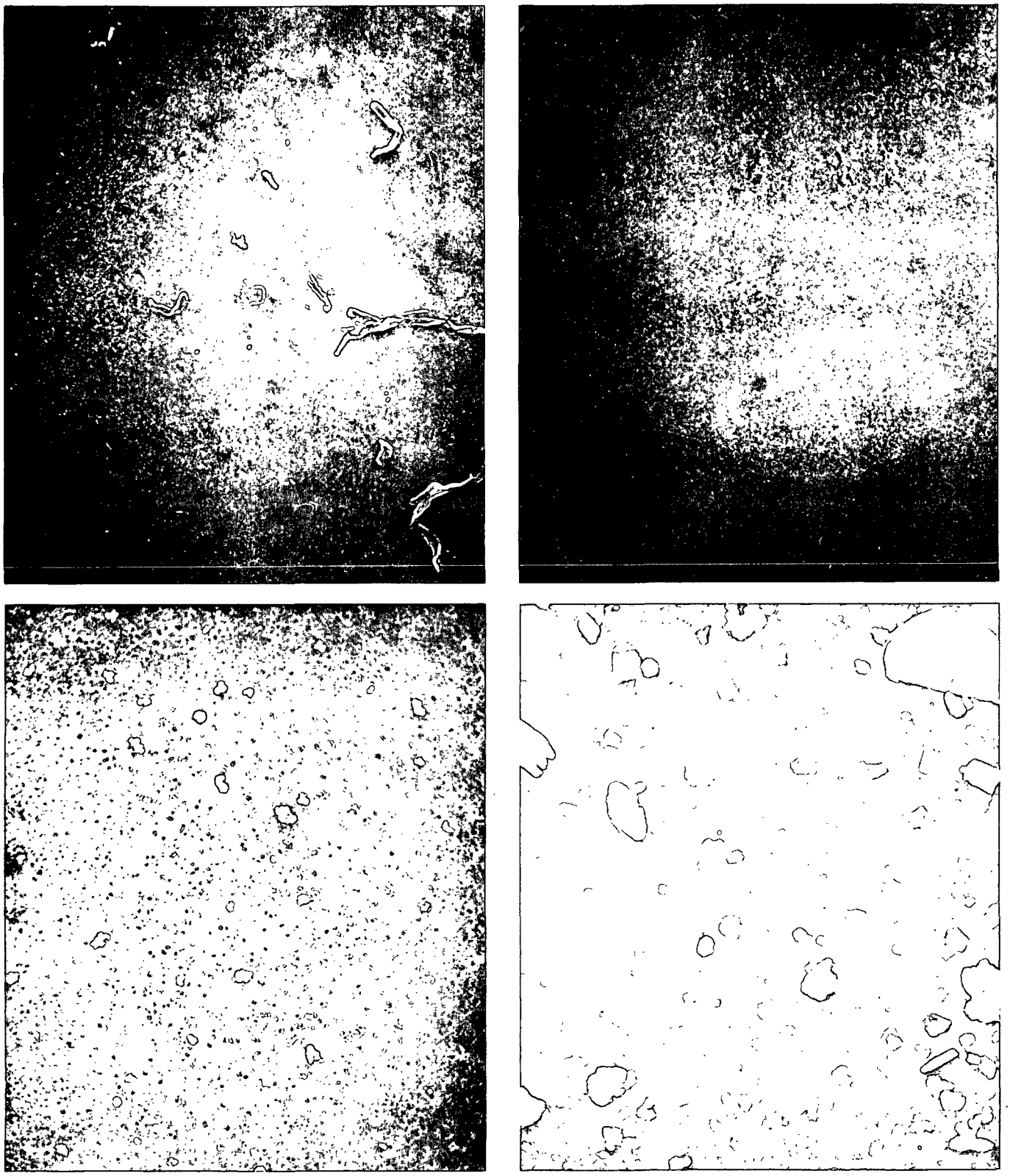


Figure 22. Scanning Electron Micrographs. (a) White Water from 445 CSF Pulp Handsheet (0.3% Consistency, no Alum, and 70 cpm) Filtered on 0.1 μm Millipore, 100X; (b) White Water from Classified Pulp Handsheet (0.3% Consistency, no Alum, and 70 cpm) Filtered on 0.1 μm Millipore, 100X; (c) TiO_2 Dispersion Filtered on 0.1 μm Millipore, 5000X; (d) Clay Dispersion Filtered on 0.1 μm Millipore, 2000X

TABLE VI

DISSOLVED ORGANIC CARBON,
AS PPM OF CO_2

Alum[a], %:	445 CSF			Classified		
	0	0.6	2.0	0	0.6	2.0
First Cycle Handsheets						
Consistency, %:		70 cpm[c]				
0.1		4	3		2	3
0.3	11	7		6	5	
		140 cpm				
0.1		5	3		2	2
0.3	11	7		7	5	
Second Cycle Handsheets						
		70 cpm				
0.1		9	5		5	3
0.3		14			9	
		140 cpm				
0.1		5	4		4	3
0.3		13			10	

[a] Based on OD weight of pulp.
[b] The accuracy of these TOC data is within ± 1 ppm.
[c] The agitator oscillates at a rate given in cycles per minute.

TABLE VII

CHEMICAL AND HYDRODYNAMIC PROPERTIES OF THE PULP

Property	445 CSF	Classified
Moisture (at 73°F, 50% RH), %	4.6	5.0
Carbohydrate[a], % OD basis		
Araban	0.04	0.05
Xylan	3.8	3.7
Mannan	7.1	7.6
Galactan	1.1	1.0
Glucan	82.5	84.2
Carboxyl, m moles/100 g OD basis		
Free[b]	3.88	3.82
Total[c]	3.98	4.11
Bound	0.10	0.29
Lignin[d], % OD basis	<1.0	<1.0
Extractives[e], % OD basis	0.7	<0.2
Ash[f], % OD basis	0.26	0.14
Hydrodynamic[g]		
Surface area, cm^2/g	22,200	8,450
Specific volume, g/cm^3	3.45	2.64

[a] Method: Tappi 53:257(1961).
[b] Method: TAPPI T-237 50-63 methylene blue.
[c] Method: TAPPI T-237 50-63 methylene blue after pretreatment with 0.1N HCl as in the $NaHCO_3$-NaCl method.
[d] Method: IPC method 428.
[e] Alcohol-benzene extraction (4 hours).
[f] Method: TAPPI T-211 m-58.
[g] Method: IPC constant rate filtration.

Titanium Dioxide

A water dispersible pigment grade of the anatase form of titanium dioxide, RG grade of the Glidden Company, was used. A great deal of information is available on this sample as it has been used in many studies in this laboratory, [for example (22,24,33)]. The sample was dispersed at 73% solids (320 g TiO_2 added to 127 ml distilled water) in a Hamilton Beach Malted Milk mixer for 20 minutes with a water jacketed container to maintain the temperature at about 20°C. The mixing time and amount of polyphosphate dispersant introduced by the manufacturer are sufficient to achieve maximum dispersion. The polyphosphate makes the TiO_2 particles negatively charged in the dispersion. The sample was diluted to 10% solids, the particles greater than 1 μm effective spherical diameter were allowed to settle out (according to Stokes' law), and the sample was stored at room temperature in a polyethylene bottle placed on a rack rotating at 6 rpm. The mean particle size of the material in dispersion is 0.23 μm with 95% being less than 0.4 μm. The mean particle size of the elementary particle is 0.18 μm and the nitrogen BET surface area is 9.8 m^2/g. The SEM of the particles in the dispersion can be seen in Fig. 22. The ambient moisture content is less than 1%, and the loss on ignition (850°C) is less than 1%. The desired amount of TiO_2 was added by using appropriate aliquots of the dispersion.

Filler Clay

A water dispersible filler clay, WPSD grade of the Georgia Kaolin Company, was used. This was chosen because it is a commercial grade having a mean particle size of about 1.5 μm. This size allows suitable observation of the fate of the optically effective sizes (<1.5 μm) and the larger sizes (the maximum in this filler is about 15 μm).

The clay was dispersed at 50% solids (200 g of clay and 200 ml of distilled water) in a Waring Blendor for 2 minutes. This procedure produces good dispersion without serious delamination of the clay stacks. The best dispersion, as determined by viscosity, required no additional polyphosphate dispersant. The dispersions were made fresh each Monday and stored on the rotating rack for use through the week. The SEM view of the particles in the dispersion can be seen in Fig. 22. The desired amount of clay was added by using appropriate aliquots of the dispersion.

Chemicals

Reagent grade alum [$Al_2(SO_4)_3 \cdot 18\ H_2O$] was used. A 10% by weight solution was made and appropriate aliquots were taken from this stock solution. Adjustments in the furnish pH were made with solutions of 1% NaOH or 2% H_2SO_4.

HANDSHEET PREPARATION

Equipment

It was desired to make paper from a furnish with consistencies near that found in headboxes, under controlled agitation, and with white water recovery. The IPC Web Former was considered, but rejected because it required too much pulp for the fines-free pulp system to be practical, and the maximum consistency to the wire was less than 0.3%. It was felt that by suitable modification of the Rapid Köthen sheet mold (Louis Schopper, Leipzig, Germany, U.S. pat. 1,995,586), the desired needs could be satisfied.

The basic components of this handsheet machine are presented in Fig. 23. Stainless steel was used where possible and the remaining brass parts were covered with plastic sheets where feasible in order to minimize the introduction of metal ions into the furnish and white water. The agitator consisted of four paddles set 90° from each other, and was centered in the deckle box about 1/4 inch from the wire.

It was driven by a controlled speed motor mechanically arranged to produce an oscillating motion covering a sweep angle of 60°.

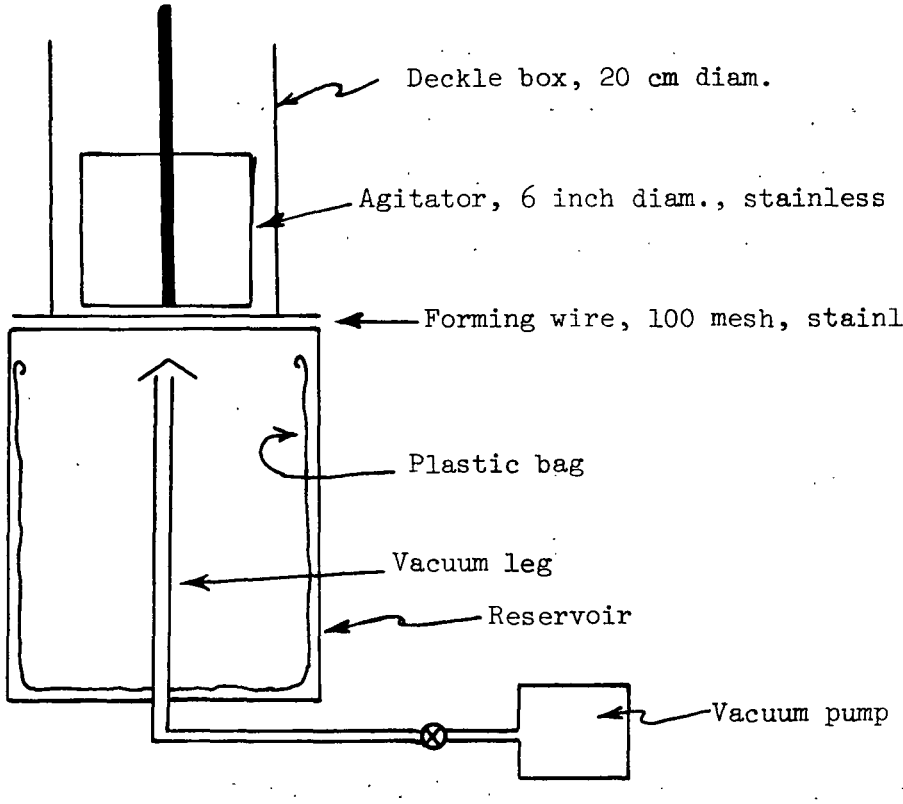


Figure 23. Diagram of the Rapid Köthen Sheet Mold with Agitator

To make a handsheet: (1) with the agitator removed, seal the wire (100 mesh stainless steel) with a small quantity (10 ml) of white water — i.e., create an air lock under the wire, (2) add the furnish to the deckle box, (3) put the agitator in place, (4) agitate at the desired speed for 15 seconds, (5) stop the agitation and immediately turn on the vacuum to drain the furnish on the wire, (6) remove the agitator and deckle box, and (7) couch, press, and dry the sheet. In this manner, sheets of 70 g/m^2, with formation suitable for optical measurements, could be made at consistencies up to 0.3% and up to agitation rates of 140 cycles per minute. At 0.3% consistency, the 2.0 g handsheets (70 g/m^2) made in this study required 667 ml of furnish, which made a depth of about 7/8 inch in the deckle box.

Sheets made from furnishes up to 1% consistency (1/4 inch depth in the deckle box) were suitable for retention measurements but not for optical measurements.

Procedure

The procedure was as follows. First cycle: a quantity of 10.0 g OD basis of pulp was dispersed in 960 ml of distilled water by placing it under a vacuum with stirring (magnetic) for ten minutes. The pulp was then diluted further with distilled water to the desired consistency (usually 0.1 or 0.3%). The order of addition was alum followed by filler, as needed, with five minutes of stirring between each addition. The pH of the slurry was then adjusted to 5.0. Handsheets were prepared (a new plastic bag was placed in the reservoir for a set of handsheets). Sufficient furnish to form a 2.0 g handsheet (2,000 ml of 0.1% or 667 ml of 0.3%) was metered into the mold for each sheet. No sealing water was used to form the first sheet and the white water from this first sheet was syphoned from the reservoir for use as sealing water for the remaining handsheets of the set. After the furnish was metered into the mold, it was agitated at 70 or 140 cpm for 15 seconds then drained on the wire. The pressure drop generating the drainage was not discernible, <20 mm Hg. The sheet was couched off the wire with 2 blotters and the use of a 1800 g couch roll. Eight handsheets were made. The sheets were then pressed between blotters at 50 psi for 5 minutes and then dried against one blotter sheet side up on the drum drier at 3.5 lb of steam pressure for 7 minutes. The white water was then syphoned from the reservoir into a polyethylene jug for use in the next cycle and for further analysis. Second cycle: a quantity of 10.0 g OD basis of pulp was dispersed in enough of the previous cycle white water to achieve the desired consistency (10.0 liters for 0.1% and 3.3 liters for 0.3%) using the vacuum-stirring-for-ten-minutes method. The same amount of alum used in the first cycle was added and the pH was adjusted to 5.0. No additional filler is

added as the concern is with the filler carried in the white water. The rest of the procedure is as in the first cycle with the handsheet set consisting of four.

ANALYSIS OF HANDSHEETS

Titanium Dioxide

The TiO_2 content was determined by an x-ray diffraction method (34). The x-ray diffraction pattern of the sheet was recorded for both the wire side and the felt side using Cu Kα (λ = 1.5418 A) source. The ratio of the x-ray intensity of the TiO_2 peak (25.4° 2θ) to that of the cellulose peak (22.6° 2θ) was determined for each side and averaged. The TiO_2 content as weight percentage of the OD sheet weight was determined from this ratio by the linear relationship

$$T = mI \qquad (2)$$

where T is the % TiO_2, I is the x-ray intensity ratio and m is a constant equal to 7.46 $\pm$ 0.04. The value of m was calculated by least squares fit from measurements of I and the corresponding T determined by ashing the sample and correcting for the pulp ash as:

$$T = (a - a_p)\ 100 \qquad (3)$$

where a and a_p are the weight fractions of ash of the paper and the pulp, respectively. (See the following clay discussion for the ashing method.) The calculation of m is based on six samples of the 445 CSF pulp and 10 samples of the classified pulp covering combinations of the two consistencies, two alum concentrations, two loading levels, and two cycles. The a_p of the pulps, required here and in the clay calculations, were found to depend on the conditions given in Table VIII.

TABLE VIII

WEIGHT FRACTION OF ASH OF THE PULPS

Condition	445 CSF	Classified
0.1% Consistency and 2.0% alum,		
First Cycle	0.0026	0.0022
Second Cycle	0.0030	0.0034
All other consistency and alum conditions and cycles	0.0026	0.0014

The percentage retention is calculated by converting the percentage of titanium dioxide on a unit weight basis, T, to percentage on a unit fiber basis, L, where

$$L = [T/100-T]\ 100. \qquad (4)$$

The retention is then

$$R = [L/L_o]\ 100, \qquad (5)$$

where L_o is the percentage of titanium dioxide initially present on a unit fiber basis. For the first cycle L_o is the loading and for the second cycle

$$(L_o)_2 = (L_o)_1\ [1-(R_1/100)], \qquad (6)$$

where the subscripts denote the cycle, so that R_1 is the retention in the first cycle.

Clay

The clay content was determined by ashing the sample. A known quantity of oven dry weight of sample (about 1 g) in a tared crucible was placed in a muffle furnace at 850°C for about 1 1/2 hours. After cooling, the quantity of ash was

weighed. All measurements were done in duplicate with the agreement usually within 1%. The weight fraction of ash of the pure filler-clay was determined to be 0.864.

The weight percentage of clay in the sheet, C, was calculated by the equation

$$C = [(a - a_p)/0.864]\ 100 \qquad (7)$$

The percentage retention is calculated in a fashion similar to titanium dioxide. Convert the percentage of clay on a unit weight basis, C, to percentage on a unit fiber basis

$$L = [C/100\text{-}C]\ 100 \qquad (8)$$

and the retention is given by Equation 5 as discussed above.

Optical Measurements

A General Electric Recording Spectrophotometer was used to determine R_o, the reflectance of a single sheet, and R_∞, the reflectance of an infinite stack of sheets, at wavelengths of 457 and 572 μm. These wavelengths were chosen because they are the wavelengths of the maximum intensity of the spectral band used to determine brightness and opacity, respectively. Eight regions of measurement were selected from at least two handsheets in the set. The basis weight of each region (3.71 cm^2) was determined by punching it out and weighing it. If the R_o values of the eight regions agreed within 2%, then the average R_o, R_∞ and basis weight were used in the solution of the Kubelka-Munk equations to determine the scattering power, sW, specific scattering coefficient, s, absorption power, kW, and specific absorption coefficient, k, of the handsheet set (W is the basis weight of the paper). If the R_o values did not agree within 2% then sW, s, kW, and k were determined for each region and the average of these values was used for that handsheet set. This latter

condition was most often true for the classified pulp handsheets because of their poor formation.

The standard brightness and opacity were also determined for each handsheet set, for possible comparisons with other work. These data are listed in Tables IX, X, XI, and XII.

Scanning Electron Microscopy of Sheets

Selected handsheets were viewed directly by SEM. Specimens about 1/4 inch square were mounted on carbon stubs by means of two sided adhesive masking tape. The specimens were then coated with carbon-platinum. (A number of samples can be placed on one stub.) When placed in the instrument they were viewed with 20 KeV electrons. After examining many regions, micrographs were made of representative regions.

ANALYSIS OF WHITE WATER

Zeta Potential of Colloidal Particles

The zeta potential was determined within several hours after the white water had been made using a Zeta Meter (Model B, Zeta Meter Inc., New York). The velocity of ten particles at the appropriate condition was measured under a known potential gradient. Using the average of this velocity and the measured conductivity, the zeta potential was determined from the Zeta Meter charts for the solution of the classical Smoluchowski equation.

Suspended Solids

The amount of suspended solids was determined by filtering an aliquot of 250 ml of white water (or less if it filtered slowly) through a tared Millipore filter (47 mm dia.) having a 0.1 μm average pore size. The Millipore filter with

TABLE IX

TAPPI OPACITY[a] FOR THE HANDSHEET WITH 445 CSF PULP

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[b]	Loading[c]				TiO_2				
0	0								
	5					78.3,*79.6	79.6	*81.4	
	15					*78.7, 81.3			
1	0	79.1	79.3	79.7	79.3				
	5	88.5	87.3	82.3	83.7				
	15	93.6	93.3	86.9	87.3				
3	0	79.0	78.3	79.2	78.7	79.6	78.3	80.1	78.8
	5	88.8	87.4	82.9	83.7	*88.5,88.8,88.8	87.8,88.9	82.5	82.4
	15	94.0	93.3	87.1	87.6	94.0,93.6,93.9	94.2	86.4	86.9
					Clay				
0	0								
	10					*80.2,*78.8		*79.6	
	25								
1	0								
	10	81.9	81.3	81.4	*80.1				
	25	*83.7	82.9	*83.3	83.4				
3	0								
	10	82.8	82.4	81.1	81.0	*83.0,*82.0	81.3	*82.0	*81.4
	25	85.3	85.3	84.4	83.3	86.4,85.9	*81.9	84.8	*82.9
10	0					*73.6[d]		74.9[d]	
	10					82.0			
	25								

[a] The asterisks indicate that the spread of the eight individual measurements was greater than 2%.
[b] Molar concentration x 10^5.
[c] Percentage based on the OD weight of pulp.
[d] The consistency here was 0.23%.

TABLE X

TAPPI OPACITY[a] FOR THE HANDSHEETS WITH THE CLASSIFIED PULP

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[b]	Loading[c]								
					TiO_2				
0	0					*81.8,*81.6	*81.5		
	5					*82.0,*82.5		*82.0	
	15								
1	0	*83.2	82.4	*81.9	*80.0				
	5	88.4	87.8	84.8	*83.7				
	15	93.5	*92.3	*88.5	87.2				
3	0	83.4	81.9	*79.3	*82.0	*79.7	*81.8	*77.9	*80.3
	5	*88.0	*87.1	84.0	84.3	*88.2,*89.7	*86.2	85.6	85.7
	15	*90.8	91.0	87.8	87.6	*93.6, 93.6	93.6	*86.3	88.6
					Clay				
0	0								
	10					*81.6		*79.1	
	25								
1	0								
	10	81.1	*80.0	*80.2	*80.5				
	25	*83.1	*81.4	*79.8	81.6				
3	0								
	10	*80.8	*82.6	81.4	*78.1	*80.6	*80.7	*79.6	*82.8
	25	*80.6	81.3	*81.7	*81.0	82.3	*83.2	*83.2	*82.9
10	0					*79.1		*75.4	
	10					*83.0			
	25								

[a] The asterisks indicate that the spread of the eight individual measurements was greater than 2%.
[b] Molar concentration x 10^5.
[c] Percentages based on the OD weight of pulp.
[d] The consistency here was 0.23%.

TABLE XI

STANDARD BRIGHTNESS FOR THE HANDSHEETS WITH 445 CSF PULP

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0						85.5		
	5						85.6,86.6	85.3	
	15								
1	0	85.5	85.8	84.9	85.2				
	5	89.2	89.2	85.4	86.4				
	15	91.4	91.5	87.5	88.6				
3	0	85.2	85.4	84.7	84.7	85.3	85.5	84.6	84.5
	5	89.4	89.3	86.4	86.7	89.5,89.1,89.0	89.0,89.3	85.2	85.9
	15	91.6	91.5	88.5	88.4	91.8,91.2,91.4	91.5	86.8	87.7
					Clay				
0	0								
	10					84.8,85.1		84.4	
	25								
1	0								
	10	84.6	85.0	84.5	84.7				
	25	84.2	84.7	84.4	84.7				
3	0								
	10	84.1	84.9	84.4	84.7	84.5,84.4	84.6	84.7	84.3
	25	84.2	84.2	84.3	84.4	84.0,84.1	83.8	84.6	84.4
10	0					85.2		84.8	
	10					84.5			
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

TABLE XII

STANDARD BRIGHTNESS OF THE HANDSHEETS WITH CLASSIFIED PULP

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					88.0,88.8	88.3		
	5					88.2,89.0		88.6	
	15								
1	0	88.2	88.8	87.9	87.9				
	5	90.5	90.8	88.8	89.1				
	15	92.4	91.9	90.2	89.9				
3	0	88.1	87.8	87.4	88.1	87.9	88.1	87.9	88.1
	5	90.5	90.4	88.8	89.2	90.6,91.3	90.4	88.8	89.1
	15	91.8	91.5	90.1	90.0	91.8,92.5	92.3	89.7	90.1
					Clay				
0	0								
	10					88.5		88.0	
	25								
1	0								
	10	87.9	88.3	88.5	88.3				
	25	87.6	87.8	87.7	88.4				
3	0								
	10	87.6	87.3	87.4	87.8	87.7	87.3	87.4	87.5
	25	86.4	86.3	86.8	86.7	86.7	87.3	86.5	86.9
10	0					86.8		87.0	
	10					87.4			
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

solids was dried at 105°C, cooled and weighed again to get dry solid weight. The dried Millipore filter with solids was then put in a tared crucible, which was placed in an oven at 180°C for 1/2 hour to char (ash flies out at higher temperature) then into a muffle furnace at 850°C for 1 1/2-hours. It was then cooled and weighed again to get the ash weight. This was done in duplicate with the agreement usually within 1%. The clear filtrates, hereafter called the supernatant, of the duplicate analyses were combined and saved for analysis of the solubles.

A centrifugation procedure originally was used to determine the suspended solids with the TiO_2 and 445 CSF pulp. However, when this was applied to the classified pulp much of the particulate matter would not settle (indicative of the relatively small size of the self-coagulated pigment) and thus the Millipore procedure was established. These two methods gave agreement within 1% on tests with common samples, and accordingly no distinction is noted in the data presented herein.

The amount of pulp fines, F, in one liter of the white water with the TiO_2, was calculated by the relationship

$$F = (w - w_a) \frac{1000}{v} \qquad (9)$$

where w and w_a are the weights of oven dry solids and the ash, respectively, in the aliquot volume, v, and F is in g per 1000 ml of white water. When no filler is present, the relationship becomes

$$F = \frac{w\ 1000}{v}, \qquad (10)$$

and when clay is the filler the relationship is

$$F = [w - (w_a/0.864)] \frac{1000}{v}. \qquad (11)$$

Ions in the Supernatant

The amounts of Al and Cu ions in solution were determined by atomic absorption spectrometry. Aliquots of 100 ml of supernatant were acidified and evaporated down to 25 ml. All samples, standards and blanks were equated to 1000 ppm Na. The limits of detection of Al ranged from 0.10 to 0.25 ppm and for Cu, 0.006 ppm.

The amount of SO_4 ion was determined by turbidimetric analysis following the method given by Standard Methods for the Examination of Water and Wastewater, 15th Edition, p. 334 (1971).

Scanning Electron Microscopy of Suspended Solids

The suspended solids in the white water were directly viewed with the Scanning Electron Microscope. A method was developed which produced a minimum of disturbance from their initial state in the white water. To accomplish this, 2 ml of the white water was diluted 5:1 with its supernatant and two ml of this sample was then filtered through a Millipore filter of 47 mm dia. having a 0.1 μm average pore size. The dilution is necessary to reduce the number of particles covering the filter, for better viewing, and the supernatant is essential as diluent to minimize colloidal changes. About 1/4 inch square pieces of the air dried Millipore filter with sample were attached to a SEM carbon stub by double sided adhesive tape and vapor coated with carbon-platinum. The specimens were viewed with 20 KEV electrons. After examining many regions, micrographs were made of representative regions.

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APPENDIX I

The following tables are compilations of the data given in graphic form in the report.

The zeta potential of the suspended solids in the white waters are given in Tables XIII and XIV.

The amounts of dissolved aluminum in the white waters are listed in Tables XV and XVI. The concentration of 3×10^{-5} molar alum is equivalent to 1.62 ppm aluminum in solution.

The amounts of dissolved sulfate ion in the white waters are listed in Tables XVII and XVIII. The concentration of 3×10^{-5} molar alum is equivalent to 8.64 ppm sulfate in solution.

The amounts of dissolved copper in the white waters are given in Tables XIX and XX.

TABLE XIII

THE ZETA POTENTIAL, mv, OF THE SUSPENDED SOLIDS
IN THE 445 CSF WHITE WATERS

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					-19.3,-16.9	-20.8		
	5					-21.6,-23.5		-18.0	
	15								
1	0	-14.6	-11.7	-15.4	-12.5				
	5	-11.3	-12.2	-11.3	-11.0				
	15	-11.0	-4.7	-12.5	-8.9				
3	0	-3.7	-8.5	-2.1	-5.0	-13.2	-15.9	-10.8	-10.8
	5	+3.8	-3.0	∿0	+2.8	-13.5,-10.0,-10.4	-11.0,-13.8	-7.4	-8.5
	15	+9.3	+5.0	+4.8	+5.4	-8.7, -8.9,-8.9	-6.1	-9.3	-9.0
					Clay				
0	0								
	10					-18.6,-20.8		-19.3	
	25								
1	0								
	10	-30.0	-25.6	-31.8	-20.8				
	25	-18.6	-14.2	-9.3	-10.2				
3	0								
	10	+18.0	+12.0	+15.4	+14.2	-15.0,-18.0	-12.2	-10.8	-7.7
	25	+11.7	+7.8	+8.6	+12.5	-13.5,-16.4	-28.6	-9.0	-24.5
10	0					-5.3[c]		-3.1[c]	
	10					∿0			
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.
[c] Consistency here was 0.23%.

TABLE XIV

THE ZETA POTENTIAL, mv, OF THE SUSPENDED SOLIDS IN THE CLASSIFIED PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					-20.8,-19.3	-18.0		
	5					-18.0,-15.0		-18.6	
	15								
1	0	-6.6	-6.1	-8.1	-9.0				
	5	+17.4	+15.4	+9.0	+15.4				
	15	+23.5	+28.6	+15.4	+22.5				
3	0	+8.0	+13.5	+12.5	+15.9	+4.5	+7.3	+5.4	+5.2
	5	+17.4	+18.0	+17.4	+15.4	+16.9,+20.8	+18.6	+7.1	+15.0
	15	+17.4	+18.0	+17.4	+14.6	+21.6,+20.0	+20.0	+17.4	+14.6
					Clay				
0	0								
	10					-19.3		-19.3	
	25								
1	0								
	10	-7.6	-6.9	-7.6	-13.8				
	25	-8.5	-13.8	-15.9	-22.5				
3	0								
	10	+15.0	+20.8	+13.5	+18.6	+6.7	-10.6	+10.6	+10.4
	25	+20.0	+17.4	+22.5	+20.8	-6.9	-10.2	+6.6	_6.2
10	0					+7.0		+13.5	
	10					+17.4			
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

TABLE XV

THE ALUMINUM CONTENT, PPM, IN SOLUTION IN THE 445 CSF PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					<0.26,<0.16	<0.25		
	5					<0.09,<0.16		0.09	
	15								
1	0	0.27	0.27	0.33	--				
	5	<0.10	0.14	0.24	0.26				
	15	0.14	<0.10	0.17	0.22				
3	0	0.93	1.0	1.5	1.6	0.31	0.30	0.50	0.50
	5	0.60	0.63	1.1	1.3	0.24,0.26,<0.16	26,0.19	0.53	0.53
	15	0.60	0.60	1.4	1.3	0.12,0.14,<0.16	0.12	0.50	0.50
					Clay				
0	0								
	10					<0.13,<0.16		<0.13	
	25								
1	0								
	10	0.13	0.13	0.19	0.35				
	25	<0.13	0.13	<0.13	0.35				
3	0								
	10	0.34	--	0.53	1.2	0.11,<0.16	0.28	0.55	0.62
	25	0.53	0.57	1.2	1.0	0.16,<0.16	<0.13	0.22	0.38
10	0					0.79[c]		2.6[c]	
	10								
	25								
50	0					0.52[c]		1.3[c]	
	10								
	25								
150	0								
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.
[c] Consistency here was 0.23%.

TABLE XVI

THE ALUMINUM CONTENT, PPM, IN SOLUTION IN THE CLASSIFIED PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2 →				
0	0					<0.25,<0.16	<0.25		
	5					0.11,<0.16		0.09	
	15								
1	0	<0.21	<0.21	0.28	0.52				
	5	0.28	<0.21	0.41	0.38				
	15	<0.21	0.21	0.21	0.21				
3	0	0.85	0.48	1.4	0.78	0.38	0.34	0.69	0.76
	5	0.72	0.53	1.2	1.1	<0.25,0.16	<0.25	0.38	0.34
	15	0.34	0.41	0.69	0.66	0.21,<0.16	0.21	0.51	0.34
					Clay				
0	0								
	10					<0.18		0.18	
	25								
1	0								
	10	0.18	0.26	0.35	<0.18				
	25	0.23	<0.18	0.26	<0.18				
3	0								
	10	0.48	0.55	0.80	0.96	0.29	<0.18	0.55	0.29
	25	0.42	0.50	0.87	0.99	0.32	<0.18	0.41	0.35
10	0					1.4		2.1	
	10					0.84			
	25								
50	0					0.66		1.5	
	10								
	25								
150	0					1.0		<0.16	
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

TABLE XVII

THE SULFATE CONTENT, PPM, IN SOLUTION IN THE 445 CSF PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					1.4,1.2	1.2		
	5					1.4,1.2		3.9	
	15								
1	0	1.4	1.2	2.9	--				
	5	1.4	1.0	3.0	2.6				
	15	1.0	1.0	2.6	3.3				
3	0	6.8	5.2	19	16	5.4	4.6	15	16
	5	5.8	6.4	12	16	6.2,6.2,5.6	6.5,6.1	18	17
	15	6.6	6.0	16	15	6.5,6.9,6.8	6.6	16	19
					Clay				
0	0								
	10					1.9,1.7		5.8	
	25								
1	0								
	10	1.2	1.3	3.0	2.6				
	25	1.3	1.2	3.4	3.0				
3	0								
	10	5.4	--	18	17	5.3,6.8	5.1	16	16
	25	5.2	5.0	14	13	6.8,7.4	5.7	19	17
10	0					26[c]		54[c]	
	10								
	25								
50	0					140[c]		240[c]	
	10								
	25								
150	0					400[c]		840[c]	
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.
[c] Consistency here was 0.23%.

TABLE XVIII

THE SULFATE CONTENT, PPM, IN SOLUTION IN THE CLASSIFIED PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					2.0,2.6	1.8		
	5					1.9,1.2		5.3	
	15								
1	0	2.6	3.0	3.4	6.2				
	5	1.9	1.6	3.6	3.3				
	15	1.4	2.0	3.8	3.8				
3	0	6.0	6.4	14	18	8.2	7.6	24	21
	5	6.0	5.2	15	14	6.3,5.4	6.8	18	17
	15	4.7	7.0	15	15	6.8,5.9	8.4	21	25
10	0								
	5								
	15								
					Clay				
0	0								
	10					2.1,1.7		4.4	
	25								
1	0								
	10	2.2	1.4	3.3	2.3				
	25	1.1	1.2	2.4	1.4				
3	0								
	10	6.2	5.7	23	16	7.7	6.1	23	19
	25	5.4	5.7	15	19	5.8	5.8	19	16
10	0					36		39	
	10					31			
50	0					130		190	
	10								
	25								
150	0					250		700	
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

TABLE XIX

THE COPPER CONTENT, PPM, IN SOLUTION IN THE 445 CSF PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		79	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					0.043,0.66	0.038		
	5					0.060,0.080		0.11	
	15								
1	0	0.045	0.033	0.078	--				
	5	0.054	0.055	0.094	0.097				
	15	0.049	0.035	0.096	0.075				
3	0	0.048	0.045	0.10	0.095				
	5	0.051	0.045	0.10	0.11	0.084,10.12	0.10,0.10	0.20	0.21
	15	0.051	0.055	0.11	0.12	0.090,0.089,0.098	0.087	0.22	0.20
					Clay				
0	0								
	10					0.052,0.086		0.10	
	25								
1	0								
	10	0.047	0.053	0.080	0.092				
	25	0.022	0.052	0.083	0.081				
3	0								
	10	0.042	--	0.088	0.12	0.11,0.12	0.11	0.21	0.24
	25	0.051	0.057	0.10	0.11	0.098,0.11	0.099	0.21	0.20
10	0					0.14		0.26	
	10								
	25								
50	0					0.13		0.24	
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.

TABLE XX

THE COPPER CONTENT, PPM, IN SOLUTION IN THE CLASSIFIED PULP WHITE WATER

Consistency:		0.1%				0.3%			
Cycle:		1st		2nd		1st		2nd	
Agitation, cpm:		70	140	70	140	70	140	70	140
Alum[a]	Loading[b]				TiO_2				
0	0					0.041,0.051	0.050		
	5					0.042,0.056		0.10	
	15								
1	0	0.046	0.040	0.083	0.085				
	5	0.037	0.036	0.078	0.059				
	15	0.036	0.036	0.072	0.066				
3	0	0.057	0.064	0.11	0.11	0.095	0.11	0.18	0.19
	5	0.027	0.026	0.079	0.085	0.064,0.076	0.062	0.13	0.15
	15	0.032	0.043	0.078	0.084	0.082,0.080	0.080	0.14	0.16
10	0								
	5								
	15								
					Clay				
0	0								
	10					0.084		0.10	
	25								
1	0								
	10	0.046	0.057	0.082	0.081				
	25	0.054	0.069	0.090	0.082				
3	0								
	10	0.043	0.043	0.084	0.086	0.066	0.063	0.16	0.13
	25	0.015	0.012	0.065	0.039	0.080	0.093	0.11	0.18
10	0					0.12		0.22	
	10					0.067			
	25								
50	0					0.11		0.22	
	10								
	25								
150	0					0.11		0.064	
	10								
	25								

[a] Molar concentration x 10^5.
[b] Percentage based on the OD weight of pulp.